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Elimination of HX (X = Cl, Br) from Haloalkenes on the Ru_2Q_2 (Q = S, Se) Core Complex

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Treatment of $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}Q_2)](CF_3SO_3)_4$ (**1**, Q = S; **2**, Q = Se) with haloalkenes resulted in the formation of complexes carrying unsaturated C_3Q_2 five-membered or C_4Q_2 six-membered rings via elimination of HX (X = Cl, Br). The reactions of **1** and **2** with allyl bromide gave the corresponding addition products, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}\overline{QCH{=}CHCH_2Q})](CF_3SO_3)_4$ (**3**, Q = S; **4**, Q = Se), via elimination of HBr. The elimination process seems to be thermodynamically controlled and takes place at the final stage of the reaction. The steric effect of the halogen atoms seems more operative than the electronic one.

Introduction

As a synthetic route to a C=C double bond in the target molecule, elimination of HX (X = halogen) from a halo-substituted compound has been utilized.[1] Such reactions are usually carried out under basic conditions, and appropriate base is added to trap the acid in order to accelerate the reaction. High-valent electron-deficient transition metal complexes are known to act as Lewis-acidic reagents. We have developed the chemistry of disulfide and diselenide bridged dinuclear Ru^{III} complexes, $[\{RuCl(P(OCH_3)_3)_2\}_2(\mu\text{-}Q_2)(\mu\text{-}Cl)_2]$ (Q = S and Se), and the chloride-abstracted tetracationic complexes, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}Q_2)](CF_3SO_3)_4$ (**1**, Q = S; **2**, Q = Se).[2] These complexes are expected to act as Lewis acids due to the relatively high valent Ru^{III}. Complexes **1** and **2** show a variety of C−S bond formation reactions with ketones,[3] alkenes,[4] alkynes,[5] and dienes[6] on the bridging dichalcogenide ligands. Except for dienes, the reactions are initiated by the activation of the appropriate C−H bond. The behavior of the cleaved hydrogen atom depends on the substrate; i.e., the hydrogen atom is liberated as a proton in the reaction with ketones, whereas in the reactions with alkenes and alkynes, the C−H activation proceeds via metathesis between the bridging dichalcogenide ligand and the allylic or propargylic C−H bond, and the hydrogen atom is usually transferred onto the C=C double or C≡C triple bond. The proton-liberation reaction of ketones suggests Lewis-acidic character of **1** and **2**; however, the deprotonated ketonyl group binds not to the metal but to the disulfide ligand to form a C−S bond.[3] In the present study, however, **1** and **2** were found to induce liberation of HX from halo-substituted alkenes.

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Experimental Section

All the reactions were carried out under an Ar or N_2 atmosphere by using the standard Schlenk line technique. Dry and oxygen-free solvents were purchased from Kanto Chemical Co. Acetonitrile-d_3 was dried over CaH_2 and distilled by trap-to-trap distillation prior to use. The reagents were purchased and used without further purification. Complexes **1** and **2** were prepared according to the procedure described in the literature.[3] 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 TMS (tetramethylsilane) 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 Material Characterization Central Laboratory in Waseda University.

Preparation of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-Se$_2$)](CF$_3$SO$_3$)$_4$ (2). Complex **2** was prepared similarly to the sulfur analogue,[2] as described in the literature,[3] i.e., [{RuCl(P(OCH$_3$)$_3$)$_2$}$_2$(μ-Se$_2$)(μ-Cl)$_2$][7] was converted to the acetonyl complex [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_2$}(μ-SeSeCH$_2$COCH$_3$){Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}](CF$_3$SO$_3$)$_3$, which was subsequently decomposed by acid to **2**.

[{RuCl(P(OCH$_3$)$_3$)$_2$}$_2$(μ-Se$_2$)(μ-Cl)$_2$] (399 mg, 0.40 mmol) and AgCF$_3$SO$_3$ (417 mg, 1.62 mmol) were dissolved into the mixture of CH$_3$CN (2 mL) and acetone (4 mL), and the solution was stirred for 3 h at room temperature. The resulting mixture was centrifuged to remove AgCl, and the supernatant was evaporated to dryness in vacuo. The beige residue was washed with Et$_2$O (10 mL × 2) and THF (10 mL) to give the acetonated complex. This crude product was dissolved in CH$_3$CN (2 mL), and the solution was treated with CF$_3$SO$_3$H (0.05 mL) with stirring for 1 h at room temperature. After evaporation to dryness in vacuo, the residue was washed with Et$_2$O (10 mL × 2) to give the dark blue powder of **2** (609 mg, 0.36 mmol, 90%). Anal. Calcd for C$_{28}$H$_{54}$F$_{12}$N$_6$O$_{24}$P$_4$Ru$_2$S$_4$Se$_2$: C, 19.79; H, 3.20; N, 4.95. Found: C, 19.59; H, 3.07; N, 4.63. ^{1}H NMR (270 MHz, CD$_3$CN): δ 3.84 (vt, $^3J_{PH}$ = 81 Hz, 36H, P(OC*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (109 MHz, CD$_3$CN): δ 115.15(s). UV−vis [CH$_3$CN, λ_{max} (nm) (ϵ_{max} (cm^{-1}M^{-1}))]: 704 (1.04 × 10^4), 515 (9.19 × 10^2), 338 (5.56 × 10^3).

Synthesis of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-QCH=CHCH$_2$Q)](CF$_3$SO$_3$)$_4$ (3, Q = S; 4, Q = Se). To a CH$_3$CN (1.5 mL) solution of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-S$_2$)] (CF$_3$SO$_3$)$_4$ (**1**)[3] (126 mg, 0.078 mmol) was added allyl bromide (0.5 mL), and the solution was stirred at ambient temperature for 12 h, before removal of the volatiles under reduced pressure. The remaining solid was washed with Et$_2$O (6 mL) and dried in vacuo. The residue was recrystallized from CH$_3$CN/DME (dimethoxyethane) to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SCH=CHCH$_2$S)](CF$_3$SO$_3$)$_4$ (**3**) as yellow crystals in 55% yield (51.8 mg, 0.043 mmol). Anal. Calcd for C$_{34}$H$_{64}$F$_{12}$N$_6$O$_{25}$P$_4$Ru$_2$S$_6$: C, 22.63; H, 3.55; N, 5.11. Found: C, 22.60; H, 3.51; N, 4.77. ^{1}H NMR (CD$_3$CN, 270 MHz, rt): δ 1.95 (s, 12H, 4C*H*$_3$CN), 2.48 (s, 3H, C*H*$_3$CN), 2.49 (s, 3H, C*H*$_3$CN), 3.83−3.88 (m, 36H, P(OC*H*$_3$)$_3$), 4.21 (ddd, J = 17, 4, and 1 Hz, 1H, SC*H*H′), 4.55 (dt, J = 17 and 2 Hz, 1H, SCH*H*′), 6.39 (dd, J = 6 and 2 Hz, 1H, SC*H*=CH), 6.80 (m, 1H, SCH=C*H*). ^{31}P{^{1}H} NMR (CD$_3$CN, 109 MHz, rt): δ 125.2 and 126.1 (d, $^2J_{PP}$ = 76 Hz), 125.5 and 125.8 (d, $^2J_{PP}$ = 77 Hz).

Analogously, the reaction of **1** (80.3 mg, 0.050 mmol) with allyl chloride (0.4 mL) gave **3** (48.7 mg, 0.029 mmol, 59%).

Similar reaction of **2** (110 mg, 0.065 mmol) with allyl bromide gave [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH=CHCH$_2$Se)](CF$_3$SO$_3$)$_4$ (**4**) in 63% yield (70.4 mg, 0.040 mmol). Anal. Calcd for C$_{31}$H$_{58}$F$_{12}$N$_6$O$_{24}$P$_4$Ru$_2$S$_4$Se$_2$: C, 21.41; H, 3.36; N, 4.83. Found: C, 21.31; H, 3.52; N, 4.71. ^{1}H NMR (CD$_3$CN, 270 MHz, rt): δ 1.95 (s, 12H, 4C*H*$_3$CN), 2.45−2.57 (m, 6H, 2C*H*$_3$CN), 3.82−3.87 (m, 36H, P(OC*H*$_3$)$_3$), 4.33 (ddd, J = 16, 4, and 1 Hz, 1H, SeC*H*H′), 4.71 (dt, J = 16 and 2 Hz, 1H, SeCH*H*′), 6.60 (dd, J = 6 and 2 Hz, 1H, SeC*H*=CH), 7.46 (m, 1H, SeCH=C*H*). ^{31}P{^{1}H} NMR (CD$_3$CN, 109 MHz, rt): δ 127.0 and 127.7 (d, $^2J_{PP}$ = 75 Hz), 127.0 and 127.9 (d, $^2J_{PP}$ = 80 Hz).

Synthesis of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH$_2$CHClSe)](CF$_3$SO$_3$)$_4$ (5). To a CH$_3$CN (2 mL) solution of **2** (164 mg, 0.096 mmol) was added allyl chloride (0.1 mL), and the solution was stirred at room temperature for 12 h. The reaction solution became dark yellow, whereupon Et$_2$O (15 mL) was added to give the precipitate. The supernatant was removed via a syringe, and the residue was washed with DME (5 mL) and dried under reduced pressure. The residue was recrystallized from CH$_3$CN/DME to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH$_2$CHClSe)](CF$_3$SO$_3$)$_4$ (**5**) as yellow crystals in 55% yield (94.6 mg, 0.053 mmol). Anal. Calcd for C$_{31}$H$_{59}$F$_{12}$N$_6$O$_{24}$P$_4$Ru$_2$S$_4$Se$_2$: C, 20.97; H, 3.35; N, 4.73. Found: C, 20.93; H, 3.02; N, 4.33. ^{1}H NMR (CD$_3$CN, 270 MHz): δ 1.95 (s, 12H, 4C*H*$_3$CN), 2.53 (s, 6H, 2C*H*$_3$CN), 3.37 (m, 1H, SeCH$_2$C*H*H′), 3.73 (m, 1H, SeCH$_2$CH*H*′), 3.81−3.92 (m, 36H, P(OC*H*$_3$)$_3$), 3.84 (m, 1H, SeC*H*H′), 4.11(m, 1H, SeCH*H*′), 6.32(t, J = 4 Hz, 1H, SeC*H*Cl). ^{13}C{^{1}H} NMR (CD$_3$CN, 67.9 MHz): δ 4.49 (2*C*H$_3$CN), 42.4 (Se*C*H$_2$), 49.1 (SeCH$_2$*C*H$_2$), 55.2−56.3 (m, P(O*C*H$_3$)$_3$), 72.7 (Se*C*HCl), 128.8−129.5 (2CH$_3$*C*N). ^{31}P{^{1}H} NMR (CD$_3$CN, 109 MHz): δ 125.4 and 127.1 (d, $^2J_{PP}$ = 68 Hz), 126.1 and 126.4 (d, $^2J_{PP}$ = 75 Hz).

Synthesis of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SCH$_2$CH=CHCH$_2$S)](CF$_3$SO$_3$)$_4$ (6). To a CH$_3$CN (1 mL) solution of **1** (346 mg, 0.22 mmol) was added 4-bromo-1-butene (0.5 mL). After stirring of the reaction mixture for 12 h, Et$_2$O (24 mL) was added to give a pale green precipitate, which was recrystallized from CH$_3$CN/CH$_2$Cl$_2$/DME to give yellow crystals of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SCH$_2$CH=CHCH$_2$S)](CF$_3$SO$_3$)$_4$ (**6**) in 55% yield (196 mg, 0.12 mmol). Anal. Calcd for C$_{32}$H$_{60}$F$_{12}$N$_6$O$_{24}$P$_4$Ru$_2$S$_6$: C, 23.16; H, 3.64; N, 5.06. Found: C, 23.23; H, 3.51; N, 4.77. ^{1}H NMR (CD$_3$CN, 270 MHz): δ 1.95 (s, 12H, 4C*H*$_3$CN), 2.49 (s, 6H, 2C*H*$_3$CN), 3.74 (m, 2H, SC*H*H′), 3.87 (vt, $^3J_{PH}$ = 6 Hz, 36H, P(OC*H*$_3$)$_3$), 4.07 (m, 2H, SCH*H*′), 6.28 (d, J = 2 Hz, 2H, SCH$_2$C*H*). ^{31}P{^{1}H} NMR (CD$_3$CN, 109 MHz): δ 125.1 (s).

Analogously, the reaction of **2** (107 mg, 0.063 mmol) with 4-bromo-1-butene gave [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH=CHCH$_2$Se)](CF$_3$SO$_3$)$_4$ (**7**) (80.2 mg, 0.046 mmol, 73%). The reaction of **2** (103 mg, 0.061 mmol) with 3-chloro-1-butene in CH$_3$CN also gave **7** (62.9 mg, 0.036 mmol, 59%). Anal. Calcd for C$_{32}$H$_{60}$F$_{12}$N$_6$O$_{24}$P$_4$Ru$_2$S$_4$Se$_2$: C, 21.92; H, 3.45; N, 4.79. Found: C, 21.45; H, 3.24; N, 4.54. ^{1}H NMR (CD$_3$CN, 270 MHz): δ 1.95 (s, 12H, 4C*H*$_3$CN), 2.51 (s, 6H, 2C*H*$_3$CN), 3.73 (m, 2H, SeC*H*H′), 3.86 (vt, $^3J_{PH}$ = 9 Hz, 36H, P(OC*H*$_3$)$_3$), 3.93 (m, 2H, SeCH*H*′), 6.40 (t, J = 2 Hz, 2H, SeCH$_2$C*H*). ^{31}P{^{1}H} NMR (CD$_3$CN, 109 MHz): δ 127.3 and 128.0 (d, $^2J_{PP}$ = 76 Hz).

Syntheses of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH$_2$C(CH$_3$)$_2$Se)](CF$_3$SO$_3$)$_4$ (8) and [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH$_2$C(CH$_2$)$_5$Se)](CF$_3$SO$_3$)$_4$ (9). Complex **2** (128 mg, 0.075 mmol) was dissolved in CH$_3$CN (2 mL), which was frozen in a

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dry ice/methanol bath and was degassed. After the solution was warmed to room temperature, 3-methyl-1-butene was introduced, and the solution was stirred for 2 h. After removal of the volatiles, the residue was washed with Et_2O. The oily product was recrystallized from CH_3CN/CH_2Cl_2/DME to give yellow crystals of [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2$(μ-$SeCH_2CH_2C(CH_3)_2Se$)]$(CF_3SO_3)_4$ (**8**) in 62% yield (82.4 mg, 0.047 mmol). Anal. Calcd for $C_{33}H_{64}F_{12}N_6O_{24}P_4Ru_2S_4Se_2$: C, 22.40; H, 3.65; N, 4.75. Found: C, 22.05; H, 3.65; N, 4.44. ^{1}H NMR (CD_3CN, 270 MHz): δ 1.67 (s, 3H, CH_3), 1.70 (s, 3H, CH'_3), 1.94 (s, 12H, 4CH_3CN), 2.43 (s, 3H, CH_3CN), 2.49 (s, 3H, CH_3CN), 2.77 (m, 1H, SeCCHH′), 3.41 (m, 1H, SeCCHH′), 3.74 (m, 2H, SeCH_2), 3.82−3.89 (m, 36H, P(OCH_3)$_3$). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz): δ 125.6 and 126.3 (d, $^2J_{PP}$ = 75 Hz), 126.2 and 127.3 (d, $^2J_{PP}$ = 80 Hz).

Analogously, the reaction of **2** (152 mg, 0.089 mmol) with vinylcyclohexane (0.1 mL) gave [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2$(μ-$SeCH_2CH_2C(CH_2)_5Se$)]$(CF_3SO_3)_4$ (**9**) (67.4 mg, 0.037 mmol, 42%). Anal. Calcd for $C_{36}H_{68}F_{12}N_6O_{24}P_4Ru_2S_4Se_2$: C, 23.89; H, 3.84; N, 4.64. Found: C, 23.74; H, 3.89; N, 4.69. ^{1}H NMR (CD_3CN, 270 MHz): δ 1.4, 1.6, 1.7, 2.1 and 2.2, broad (10H, C(CH_3)$_5$), 1.95 (s, 12H, 4CH_3CN), 2.50 (s, 3H, CH_3CN), 2.52 (s, 3H, CH_3CN), 2.57 (m, 1H, SeCCHH′), 3.62, (m, 1H, SeCCHH′), 3.76 (m, 2H, SeCH_2), 3.80−3.89 (m, 36H, P(OCH_3)$_3$). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz): δ 125.5 and 126.2 (d, $^2J_{PP}$ = 79 Hz), 126.2 and 126.7 (d, $^2J_{PP}$ = 79 Hz).

Synthesis of [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2${μ-$QCH_2C(=CH_2)CH_2Q$}](CF$_3$SO$_3$)$_4$ (10, Q = S; 11, Q = Se). To a CH_3CN (1 mL) solution of **1** (165 mg, 0.10 mmol) was added 3-chloro-2-methyl-1-propene (0.5 mL), and the solution was stirred for 4 h. After removal of the volatiles in vacuo, the residue was washed with Et_2O (16 mL), and the green residue was recrystallized from CH_3CN/DME to give [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2${μ-$SCH_2C(=CH_2)CH_2S$}]$(CF_3SO_3)_4$ (**10**) as yellow crystals in 61% yield (104 mg, 0.063 mmol) and another uncharacterized product(s). 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, 22.94; H, 3.42; N, 4.96. ^{1}H NMR (CD_3CN, 270 MHz): δ 1.95 (s, 12H, 4CH_3CN), 2.49 (s, 6H, 2CH_3CN), 3.83−3.88 (m, 36H, P(OCH_3)$_3$), 4.23 (d, J = 17 Hz, 2H, SCHH′), 4.61 (d, 2H, SCHH′), 5.51 (s, 2H, C=CH_2).

Analogously, the reaction of **2** (175 mg, 0.10 mmol) gave [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2$(μ-$SeCH_2C(=CH_2)CH_2Se$)]-$(CF_3SO_3)_4$(**11**) in 72% yield (130 mg, 0.074 mmol). Anal. Calcd for $C_{32}H_{60}F_{12}N_6O_{24}P_4Ru_2S_4Se_2$: C, 21.92; H, 3.45; N, 4.79. Found: C, 21.68; H, 3.37; N, 4.63. ^{1}H NMR (CD_3CN, 270 MHz): δ 1.95 (s, 12H, 4CH_3CN), 2.51 (s, 6H, 2CH_3CN), 3.82−3.88 (m, 36H, P(OCH_3)$_3$), 4.16 (d, J = 12 Hz, 2H, SeCHH′), 4.30 (d, 2H, SeCHH′), 5.29(s, 2H, C=CH_2). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz): δ 127.9 and 127.2 (d, $^2J_{PP}$ = 78 Hz).

Synthesis of [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2${μ-$SeCH_2C(=CHCl)CH_2Se$}](CF$_3$SO$_3$)$_4$ (12). To a CH_3CN (2 mL) solution of **2** (103 mg, 0.061 mmol) was added 3-chloro-2-chloromethyl-1-propene (0.1 mL), and the solution was stirred for 20 days at room temperature. The reaction solution became pale green, whereupon Et_2O (15 mL) was added to give the precipitate. The supernatant was removed via a syringe, and the residue was washed with DME (5 mL) and was dried under reduced pressure. The residue was recrystallized from CH_3CN/DME to give [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2${μ-$SeCH_2C(=CHCl)CH_2Se$}](CF$_3$SO$_3$)$_4$ (**12**) as yellow crystals in 65% yield (69.8 mg, 0.039 mmol). Anal. Calcd for $C_{32}H_{59}ClF_{12}N_6O_{24}P_4Ru_2S_4Se_2$: C, 21.50; H, 3.33; N, 4.70. Found: C, 21.20; H, 3.21; N, 4.46. ^{1}H NMR (CD_3CN, 270 MHz): δ 1.95 (s, 12H, 4CH_3CN), 2.51 (s, 6H, 2CH_3CN), 3.83−3.89 (m, 36H, P(OCH_3)$_3$), 4.29−4.44 (m, 4H, SeCH_2), 6.50 (t, J = 1 Hz, 1H, C=CHCl). ^{13}C{^{1}H} NMR (CD_3CN, 67.9 MHz): δ 4.56 (2CH_3CN), 41.2 (SeCH_2), 44.8 (Se$C'H_2$), 55.7−56.0 (m, P(OCH_3)$_3$), 122.6 (C=CHCl), 128.8−129.3 (2CH_3CN), 142.4 (C=CHCl). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz): δ 126.7 and 127.3 (d, $^2J_{PP}$ = 80 Hz), 126.5 and 127.5 (d, $^2J_{PP}$ = 80 Hz).

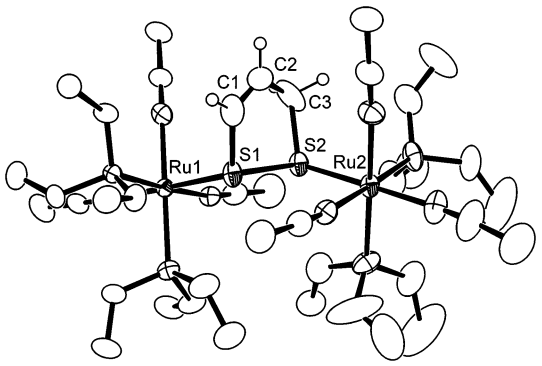
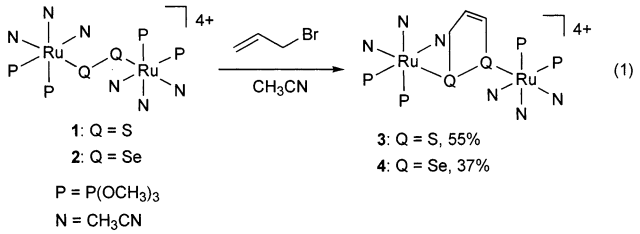


Figure 1. Structure of complex **3** (the cation part, drawn at the 50% probability level; methyl H atoms are omitted for clarity).

X-ray Diffraction Study. Diffraction data for **3**, **5**, and **8**−**12** 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 summarized in Table 1.

Result and Discussion

Treatment of [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2$(μ-Q_2)]$(CF_3SO_3)_4$ (**1**, Q = S; **2**, Q = Se) with excess allyl bromide in CH_3CN led to the gradual color change of the solution from dark blue to green. The unsaturated C_3Q_2 five-membered-ring complexes, [{Ru($P(OCH_3)_3)_2(CH_3CN)_3$}$_2$(μ-$QCH=CHCH_2Q$)]$(CF_3SO_3)_4$ (**3**, Q = S, 55%; **4**, Q = Se, 67%), were obtained as yellow crystals after recrystallization from CH_3CN/DME (eq 1).



(1)

In the ^{1}H NMR spectra of **3** and **4**, the olefin proton signals are found at δ 6.39 and 6.80 for **3**, and δ 6.60 and 7.46 for **4**, and these are assigned to the two internal olefin protons of the unsaturated C_3Q_2 five-membered ring. Figure 1 shows the X-ray structure of **3**, and the selected structural parameters of **3** are listed in Table 2.

Table 1. Crystallographic Data for **3** and **8**−**12**

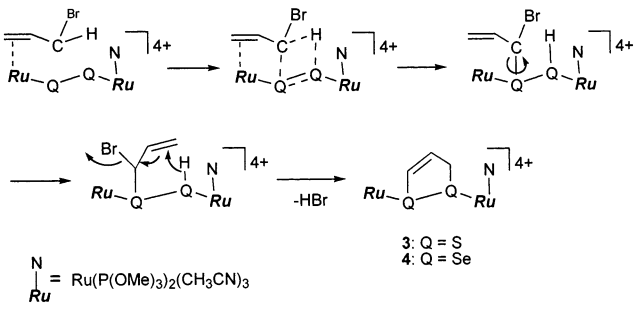
	3	**8**	**9**	**10**	**11**	**12**
empirical formula	$C_{31}H_{58}F_{12}N_6O_{24}P_4Ru_2S_6$	$C_{33}H_{64}F_{12}N_6O_{24}P_4Ru_2S_4Se_2$	$C_{36}H_{68}F_{12}N_6O_{24}P_4Ru_2S_4Se_2$	$C_{32}H_{60}F_{12}N_6O_{24}P_4Ru_2S_6$	$C_{32}H_{60}F_{12}N_6O_{24}P_4Ru_2S_4Se_2$	$C_{32}H_{59}ClF_{12}N_6O_{24}P_4Ru_2S_4Se_2$
fw	1645.21	1769.08	3618.29	1659.24	1753.04	1787.48
T (K)	293(2)	293(2)	124(2)	123(2)	124(2)	124(2)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	P_n (No. 7)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	12.421(5)	12.751(7)	12.711(3)	12.3850(17)	12.210(4)	12.217(3)
b (Å)	13.384(5)	13.084(8)	22.497(6)	13.7700(19)	14.448(5)	14.474(3)
c (Å)	19.454(7)	21.728(13)	25.779(6)	18.190(2)	18.758(6)	18.817(4)
α (deg)	105.395(7)	106.016(10)	74.749(4)	90	80.704(7)	82.398(4)
β (deg)	93.443(7)	91.271(14)	82.206(5)	95.616(2)	89.852(6)	89.546(4)
γ (deg)	93.039(7)	91.651(12)	89.915(5)	90	85.828(6)	84.426(3)
V (Å^3)	3100(2)	3481(4)	7042(3)	3087.2(7)	3256.9(17)	3282.6(11)
Z	2	2	4	2	2	2
λ (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
d_{calcd} (g cm^{-3})	1.763	1.668	3.413	1.785	1.788	1.808
μ (mm^{-1})	0.905	1.793	3.549	0.909	1.915	1.942
R1[a] [$I > 2\sigma(I)$]	0.0954	0.0936	0.0868	0.0354	0.1130	0.0857
wR2[b] [$I > 2\sigma(I)$]	0.2501	0.1607	0.2450	0.0904	0.2893	0.1880
R1 (all data)	0.1291	0.3564	0.1835	0.0371	0.1786	0.2360
wR2 (all data)	0.2916	0.2472	0.2988	0.0917	0.3337	0.2452
GOF[c]	1.012	0.815	0.956	1.029	0.979	0.915

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$. [c] $GOF = [\sum w(F_o^2 - F_c^2)/\sum(n - p)]^{1/2}$, where n = number of reflections and p = number of parameters.

Table 2. Structure Parameters for **3**

Bond Distances (Å)			
Ru(1)−S(1)	2.306(2)	S(1)−C(1)	1.743(10)
Ru(2)−S(2)	2.320(2)	S(2)−C(3)	1.837(12)
S(1)−S(2)	2.118(2)	C(1)−C(2)	1.276(18)
		C(2)−C(3)	1.450(19)
Bond Angles (deg)			
S(1)−C(1)−C(2)			116.9(9)
C(1)−C(2)−C(3)			121.4(10)
Torsion Angles (deg)			
Ru(1)−S(1)−S(2)−Ru(2)			−155.28(8)

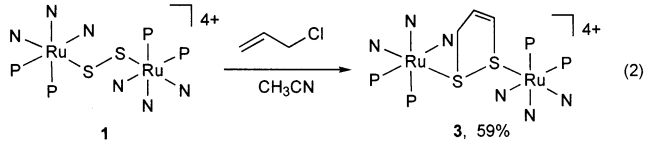
Scheme 1



The short and long C−C bond distances (1.276(18) and 1.450(19) Å) of **3** correspond to the C−C double and single bonds in the five-membered ring. The S2−C3−C2−C1 torsion angle (17.5(17)°) indicates that these atoms sit approximately on a plane, and a C═C double bond exists between C3 and C2. The S−S bond distance and the Ru−S−S−Ru torsion angle are comparable to those in the previously reported saturated C_3S_2 five-membered ring complex $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}\overline{SCH_2CH_2CHRS})](CF_3SO_3)_4$.[4]

In addition to the previous C−S bond formation reactions via C−H bond activation,[2−5] the present study has proved that HBr elimination takes place on the disulfide ligand. The plausible mechanism is shown in Scheme 1, in which the first step of the allylic C−H bond cleavage and the subsequent rotation of the substrate around the C−S bond are analogous to what was observed in alkene reactions.[4] The present reactions show that the organic molecule bound to the dichalcogenide bridges of **1** or **2** with a C−S bond is still activated and undergoes subsequent transformation processes involving the HX elimination reaction. Similarly, elimination of H_2O is observed in the reactions of hydroxyl-substituted alkenes and alkynes.[8]

The reaction of **1** with allyl bromide and allyl chloride gave an identical product **3** (eqs 1 and 2). For the disulfide

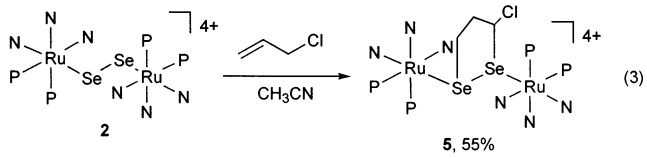


(2)

complex **1**, the difference of the halogens does not affect the reaction pattern; however, the reaction of the diselenide complex **2** with allyl chloride and allyl bromide gave

(8) Moriya, Y.; Hatemata, S.; Sugiyama, H.; Matsumoto, K. Submitted.

different products; the reaction with allyl bromide gave product **4** analogous to **3**, whereas the reaction with allyl chloride gave a different type of compound [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH$_2$CHClSe)](CF$_3$SO$_3$)$_4$ (**5**) in 55% yield (eq 3). This difference is explained by the steric



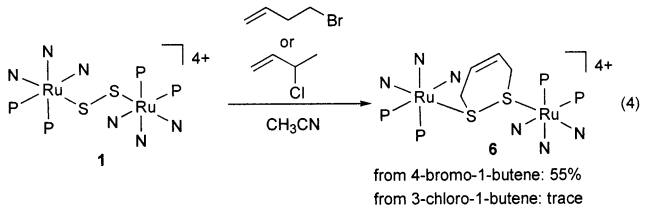
(3)

bulkiness of the bromide relative to the chloride. The wide reaction space of the RuSeSeRu core compared to RuSSRu allows accommodation of the chloride without losing the chloride atom until the end of the reaction as in eq 3. This reaction corresponds to what is expected and is analogous to the reactions with propylene and other alkenes.[4] However, having the less spacious RuSSRu core, **1** cannot accommodate the chloride ligand and HCl is eliminated from the ligand as in eq 1. In the reaction of **2** with allyl bromide, the bromide substrate is too bulky to retain, and at the intermediate stage, HBr is eliminated.

In the following study described below, either or both chloride and bromide substrates are used, depending on the commercial availability. According to the previous study,[3] substrates with an electron-withdrawing group are usually less reactive toward complexes **1** and **2**, and the halo-substituted ones are also relatively less reactive. In addition, the halogen atom occasionally acts as a bulky group to prevent the smooth reaction. Therefore, less bulky chloride species are in most cases used in the present study.

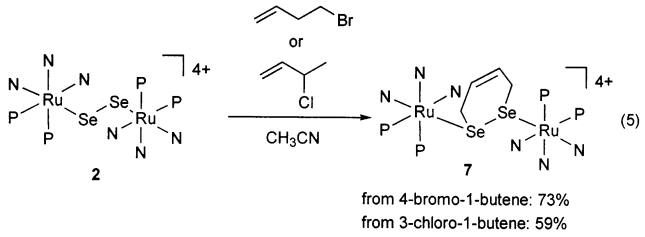
Electrophilic addition of an organic group to the sulfide ligand on a transition metal is well-known; however, elimination of HX has not been reported. For example, the reaction of [WS$_4$]$^{2-}$ with RX gave [WS$_3$(SR)]$^-$ (R = Et, ^{i}Pr, ^{t}Bu, C$_6$H$_5$CH$_2$, and C$_3$H$_5$).[9] Analogously, the reaction of [Cp*WS$_3$]$^-$ with RX gave Cp*WS$_2$(SR) (R = CH$_3$, C$_6$H$_5$CH$_2$).[10] The reaction of the bridging sulfide in [{W(CO)$_5$}$_2$(μ-S)]$^{2-}$ with RCl (R = CH$_3$CO, C$_6$H$_5$CH$_2$) gave thiolate ligand.[11] In these examples, C−S bonds are formed via carbon−halogen bond cleavage, but C−S bond formation via less reactive C−H bond cleavage is unprecedented.

Treatment of **1** with 4-bromo-1-butene results in the formation of the C$_4$S$_2$ 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$_3$)$_4$ (**6**) in 55% yield, whereas the reaction of **1** with 3-chloro-1-butene gave a trace of **6** and the Ru^{II}Ru^{III} complex [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-S$_2$)](CF$_3$SO$_3$)$_3$ as the major product (eq 4). The latter complex was reported when an acetonitrile solution of **1** was left standing. The reduction mechanism is not known.[2a,b]



(4)

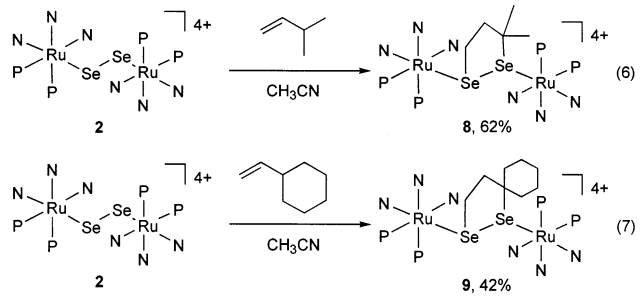
On the other hand, both 4-bromo-1-butene and 3-chloro-1-butene gave the identical compound [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH=CHCH$_2$Se)](CF$_3$SO$_3$)$_4$ (**7**) in the reaction with **2** (from 4-bromo-1-butene, 73%; from 3-chloro-1-butene, 59%) (eq 5). Previously we have reported that the



(5)

reaction of **1** with nonhalogenated alkenes proceeds via activation of the allylic C−H bond similar to Scheme 1.[3] In 4-bromo-1-butene, bromide is not attached to the allylic carbon, and the steric effect of the bromide is not significant in the reaction of **1** with 4-bromo-1-butene. In contrast, the allylic position of 3-chloro-1-butene is crowded due to the methyl and the chloride groups. In our previous study, the reaction product of **1** with 3-methyl-1-butene, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SCH$_2$CH$_2$C(CH$_3$)$_2$S)](CF$_3$SO$_3$)$_4$, was found to have two significantly different C−S bond distances (1.786(8) and 1.922(6) Å; the latter is for the C−S bond of the ternary carbon atom), which shows that the C$_3$S$_2$ five-membered ring is distorted by the steric hindrance of the two methyl groups.[4b] This fact suggests that there is steric limitation for the substrate to react with **1**. Since a 3-chloro-1-butene molecule is roughly estimated to be comparable to or a little larger than 3-methyl-1-butene in size, the reaction of 3-chloro-1-butene with **1** does not proceed smoothly. In addition, the allylic C−H bond of this substrate is deactivated due to the electron-withdrawing effect of the halogen atom, and therefore only a trace amount of the product is obtained. In contrast, the reaction of **2** with 3-chloro-1-butene is not hampered by the electronic and/or steric effect. Due to the larger size of the bridging ligand, **2** reacts readily with the bulkier substrate. Actually, no significant distortion is found in the structure of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH$_2$C(CH$_3$)$_2$Se)](CF$_3$SO$_3$)$_4$ (**8**) (eq 6), which is obtained from the reaction of **2** with 3-methyl-1-butene; the two C−Se bond distances are 1.964(11) and 2.034(13) Å. Furthermore, **2** readily reacts with much bulkier vinylcyclohexane to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SeCH$_2$CH$_2$C(CH$_2$)$_5$Se)](CF$_3$SO$_3$)$_4$ (**9**) (eq 7). It is difficult to estimate the electronic effect, whereas the steric effect is readily compared between **1** and **2**. The

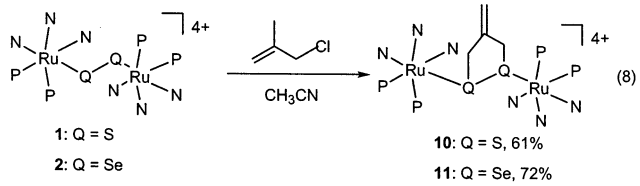
(9) (a) Boorman, P. M.; Wang, M.; Parvez, M. *J. Chem. Soc., Chem. Comuun.* **1995**, 999. (b) Kruhlak, N. L.; Wang, M.; Boorman, P. M.; Parvez, M.; McDonald, R. *Inorg. Chem.* **2001**, *40*, 3141.
(10) Kawaguchi, H.; Tatsumi, K. *J. Am. Chem. Soc.* **1995**, *117*, 3885.
(11) Angelici, R. J.; Gingerich, R. G. W. *Organometallics* **1983**, *2*, 89.



mechanism of the previously reported reactions with nonhalogenated alkenes was based on the methathesis between the allylic C−H bond and the bridging dichalcogenide, and the reaction pattern was strongly affected by the steric effect.[5]

As for the mechanism of the reactions in eqs 4 and 5, several pathways are conceivable based on Scheme 1, but they are yet speculative and it would not be suitable to show them in the present paper.

In the previous study on the reaction of **1** with alkenes, the reaction products were not easy to isolate when the substrates were geminally disubstituted alkenes such as isobutene and 2-ethyl-1-butene. When methylenecycloalkanes were used as substrates, the products were classified into two types, depending on the ring size, and were quite different from those of the simple terminal alkenes.[5] In contrast, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}QCH_2C(=CH_2)CH_2Q\}](CF_3SO_3)_4$ (**10**, Q = S, 61%; **11**, Q = Se, 72%) were readily obtained from the reactions of **1** or **2** with 3-chloro-2-methyl-1-propene (eq 8).



In the reaction of eq 8, the C=C double bond is formed via HCl elimination as the *exo*-methylene group. The reactions of 3-chloro-2-methyl-1-propene with **1** or **2** proceed more easily, compared to those with allyl bromide. The difference would be explained by the difference of the reactivity of the C−H bond in these two substrates: allyl bromide has only deactivated C−H bonds of the bromomethyl group, whereas 3-chloro-2-methyl-1-propene has two types of C−H bonds, namely, methyl and less activated chloromethyl groups, and the former is preferably activated in the reaction as shown in Scheme 2. The reaction is initiated by the activation of the methyl C−H bond, and the chloride is liberated from the chloromethyl group to form the *exo*-methylene groups in **10** and **11**.

The structures of **10** and **11** are determined by X-ray diffraction analysis. Figure 2 shows the structure of **11**, and the selected structural parameters of **10** and **11** are compared in Table 3.

As an extended study, the reactions of **1** and **2** with 3-chloro-2-chloromethyl-propene were examined. Only **2** reacts with the substrate to give $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}SeCH_2C(=CHCl)CH_2Se\}](CF_3SO_3)_4$ (**12**) in 65% yield after 20 days of reaction (eq 9).

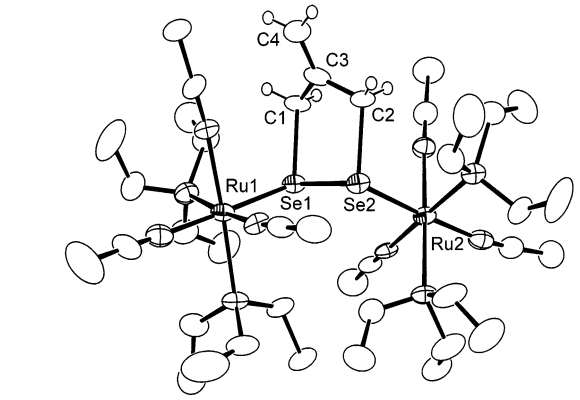


Figure 2. Structure of complex **10** (the cation part, drawn at the 50% probability level; methyl H atoms are omitted for clarity).

Scheme 2

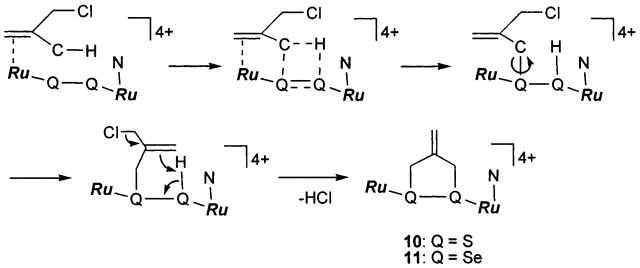
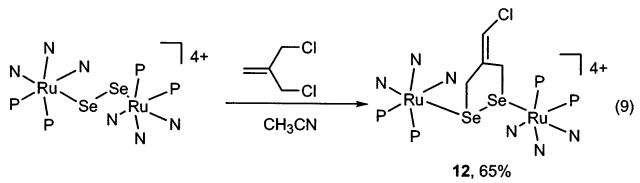


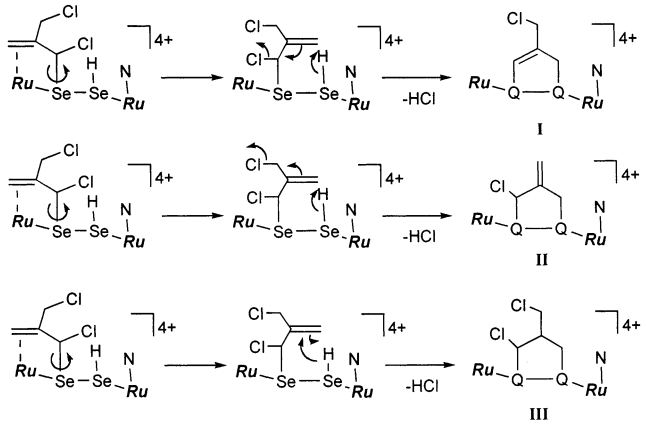
Table 3. Structure Parameters for **11** and **12**

	11 (Q = S)	**12** (Q = Se)
Bond Distances (Å)		
Ru(1)−Q(1)	2.3458(10)	2.4574(15)
Ru(2)−Q(2)	2.3355(10)	2.4350(15)
Q(1)−Q(2)	2.1155(14)	2.4212(17)
Q(1)−C(1)	1.809(5)	1.968(11)
Q(2)−C(3)	1.806(5)	1.998(11)
C(1)−C(2)	1.452(7)	1.491(17)
C(2)−C(3)	1.468(7)	1.482(17)
C(2)−C(4)	1.405(7)	1.327(17)
Bond Angles (deg)		
C(1)−C(2)−C(3)	117.1(4)	116.3(11)
C(1)−C(2)−C(4)	122.4(6)	122.4(12)
C(3)−C(2)−C(4)	120.4(5)	121.3(12)
Torsion Angles (deg)		
Ru(1)−Q(1)−Q(2)−Ru(2)	166.53(4)	143.19(5)



In the reaction of eq 9, the initial C−H bond activation must occur at the less activated chloromethyl group. The steric hindrance of the chloride on the allylic position would not affect seriously the reaction of **1**, since **1** can react with allyl bromide. The steric hindrance of another chloromethyl group would also be negligible in the reaction with **1**. Since any steric reason to hinder the reaction of **1** cannot be found,

Scheme 3



the difference of the reactivity between **1** and **2** would be due to the electronic reason. Compound **2** would have higher reactivity toward less activated substrates. On the other hand, the reaction pattern of the HCl elimination in the reaction of eq 9 cannot be explained in analogy to the previous reactions. If the present reaction corresponds to the reaction of **2** with allyl bromide, a type I structure in Scheme 3 is expected, whereas if the reaction corresponds to the reaction of **2** with 3-chloro-2-methyl-1-propene, a type II structure is expected. If the elimination of HCl does not occur, a type III structure is expected (Scheme 3). However, the actually crystallographically confirmed structure of **12** shown in Figure 3 differs from all three.

The structure of **12** was obtained after three attempts at X-ray crystallographic analysis. In the first two structural analyses, crystals were obtained after the reaction for 1 day; however, it was too difficult to confirm the structure of the product due to the complicated disorder of the Cl atoms. The incomplete structure seems to be a superimposition of a few species containing two Cl atoms. This is also supported by the elemental analysis. (Anal. Calcd for $C_{32}H_{58}Cl_2F_{12}N_6O_{24}P_4Ru_2S_4Se_2$: C, 21.10; H, 3.21; N, 4.61. Found: C, 21.05; H, 3.26; N, 4.47.) One of the species seems to have a type III structure. The elimination of HCl takes place after cycloaddition, and the subsequent reaction proceeds thermodynamically to give the most stable structure of **12**. In the ^{1}H NMR spectrum of **12**, the olefin proton resonance is observed at δ 6.50, and gives the cross peak with the methyne ^{13}C resonance at δ 122.6 in the ^{1}H{^{13}C} HMQC spectrum, and also the cross peak with the ^{13}C resonance at δ 142.3 in the ^{1}H{^{13}C} HMBC spectrum.

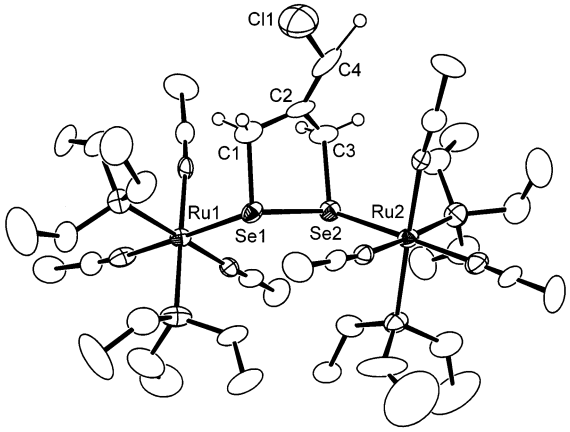


Figure 3. Structure of complex **12** (the cation part, drawn at the 50% probability level; methyl H atoms are omitted for clarity).

The selected structural parameters are listed in Table 3, together with those of **10** and **11**. Except for the Cl atom on the carbon atom, the structural features of **12** are identical to those of **11**.

Conclusion

The reactions of **1** and **2** with haloalkenes give a variety of addition products via elimination of HX (X = Cl, Br). The steric effect of the halogen atoms seems more operative than the electronic one. The elimination process seems to be thermodynamically controlled and takes place at the final stage of the reaction.

Acknowledgment. The financial support of CREST from Japan Science and Technology Corporation and the Grant-in-Aid for COE Research, Ministry of Education, Culture, Sports, Science and Technology (MEXT) are acknowledged.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **3**, **5**, and **8**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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