# Reactions of Hydridoruthenium(II) Complexes with Alkyl Allylic Sulfides

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(Received May 22, 1992)

$[RuClH(CO)(PPh_3)_3]$ (**1**) reacted with alkyl allyl sulfides at 10—25°C to give insertion products, $[Ru(CH_2CH_2CH_2SR)Cl(CO)(PPh_3)_2]$ ($R=CH_3$, **2**; $R=CH_2C_6H_5$, **3**; and $R=CH_2CH=CH_2$, **4**). Complexes **2**—**4** exhibited temperature-dependent NMR spectra above −40°C, indicating that rapid exchange occurred between two structural isomers owing to inversion of the alkyl group upon the coordinated sulfur stom. Upon heating at 67°C, **2** was converted into a binuclear complex, $[Ru_2(\mu\text{-}Cl)Cl(\mu\text{-}H)(\mu\text{-}SCH_3)(CO)_2(PPh_3)_3]$, evolving propylene. Complex $[RuClH(CO)(dppe)(PPh_3)]$ (**7**) [dppe=1,2-bis(diphenylphosphino)ethane] reacted with allyl methyl sulfide at 110°C to afford $[Ru_2Cl_2(\mu\text{-}SMe)_2(CO)_2(dppe)_2]$ (**8**), evolving propylene.

Insertion reactions of olefins into a Ru–H bond have been regarded as an important step in many catalytic reactions with ruthenium complexes.[1] Previously, we reported that a hydridoruthenium(II) complex $[RuClH(CO)(PPh_3)_3]$ (**1**) reacted with vinyl compounds,[2,3] conjugated dienes,[3] and dialkyl maleates[4] to give the corresponding insertion products. Allylic compounds, substituted olefins themselves, have been used in allylation reactions catalyzed by transition metal complexes.[5] Osakada et al.[6] reported that reactions of allylic aryl sulfides with $[RhH(PPh_3)_4]$ caused cleavage of allylic sulfur bond to afford $[Rh_2(\mu\text{-}SAr)_2(PPh_3)_4]$ and the corresponding olefins. In this report, we will deal with novel [3-(alkylthio)propyl-*C*$^1$,*S*]ruthenium(II) complexes formed by reactions between alkyl allylic sulfides and **1**, and with thermal reaction product of one of the complexes.

## Results and Discussion

**[3-(Alkylthio)propyl-*C*$^1$,*S*]ruthenium(II) Complexes.** Complex **1** reacted with alkyl allyl sufides ($CH_2=CH-CH_2SR$) in a THF solution at 10—28°C to afford insertion products, $[Ru(CH_2CH_2CH_2SR)Cl(CO)(PPh_3)_2]$ (R=Me, **2**; $R=CH_2C_6H_5$, **3**; and $R=CH_2CH=CH_2$, **4**). It is noteworthy that C,S-chelated propylruthenium(II) complexes were isolated from **1**, since alkylmetal complexes were postulated as intermediates in the allylic sulfur bond cleavage reactions between $[RhH(PPh_3)_4]$ or $[RuH_2(PPh_3)_4]$ and allylic aryl sulfides, but not isolated.[6] It seems likely that the stability of **2**—**4** is due to both the chelate effect of the 3-(alkylthio)propyl-*C*$^1$,*S* group and electron-delocalization among carbonyl ligand and phosphine ones, which prevents the ligands from dissociating to form a vacant site. 3-(Alkylthio)propyl-*C*$^1$,*S*-metal complexes, such as **2**—**4**, have been reported in the cases of $[Pd_2\{CH_2CR^1(OMe)CH_2SR^2\}_2Cl_2]$ ($R^1=H$ or Me, $R^2=Et$ or $Bu^t$).[7]

The IR spectra of **2**—**4** showed a strong absorption band near 1915 cm$^{-1}$, attributable to metal-bonded carbonyl group. $^1H$ NMR spectra of **2**—**4** exhibited broad signal ascribable to S-methyl or -methylene protons at room temperature and showed temperature-dependent NMR spectra above −40°C. This indicates that rapid exchange occurs between two structural isomers owing to inversion of the alkyl group upon the coordinated sulfur atom at ambienent temperature (Scheme 1). The $^{31}P\{^1H\}$ NMR spectra of **2**—**4** at −50°C showed two sets of AB type quartet with coupling constants of about 15 Hz (Table 1). These data certify that each of **2**—**4** consists of two isomers owing to the quench of the inversion of the alkyl group upon the coordinated sulfur atom at this temperature and that two $PPh_3$ ligands in each isomer are coordinated cis to each other. The $^{13}C\{^1H\}$ NMR spectra of **2**—**4** showed two carbonyl carbon resonances at $\delta=201$—205 (Table 2). Since these resonances did not exhibit a large C–P coupling, it is obvious that the carbonyl group is situated cis to the two $PPh_3$ ligands.

The $^1H$ NMR spectrum of **2** showed two doublets at $\delta=1.20$ and 1.76, ascribable to methyl protons, indicating that methylthio group was coordinated trans to one of the two $PPh_3$ ligands. The ruthenium-bonded methylene carbon of the major isomer for **3** or **4** resonated as a doublet with a comparatively large coupling constant. These data reveal that the 3-(alkylthio)propyl-*C*$^1$,*S* moiety is located trans to the two $PPh_3$ ligands, as demonstrated in Scheme 1. It is noted that the cis coordination of the two $PPh_3$ ligands is in analogy with $[Ru\{CH(CO_2R)CH_2CO_2R\}Cl(CO)(PPh_3)_2]$ derived from **1**,[4] but in sharp contrast with chelated alkylruthenium(II) complexes, such as $[Ru(CH_2CH_2C_5H_4N)Cl(CO)(PPh_3)_2]$ and $[Ru\{CH_2CH_2C(O)OMe\}Cl(CO)(PPh_3)_2]$, which have two *trans*-coordinated $PPh_3$ ligands.[3] The alkyl substituent upon the ruthenium-

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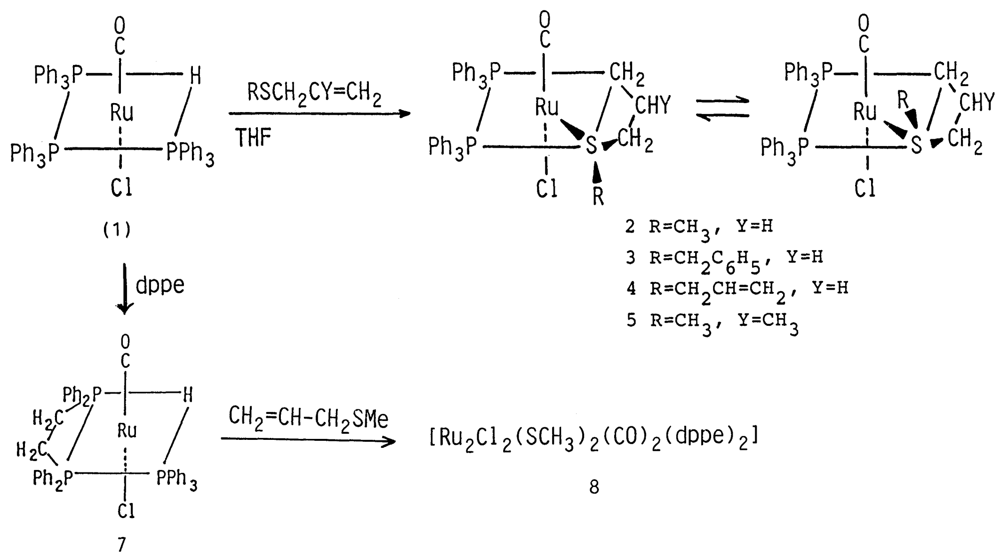

Scheme 1.

Table 1. $^1$H and $^{31}$P{$^1$H} NMR Data of the Ruthenium(II) Complexes

| Complex | $^1$H NMR[a)] | | $^{31}$P{$^1$H} NMR | | Isomer ratio |
|---|---|---|---|---|---|
| | Aliphatic moiety | Aryl moiety[b)] and Hydride | δ[c)] | $J$/Hz | % |
| **2a** | 1.20 (d, 2.2, $SCH_3$)[d)] | 7.21 (t, 8, *m*-H), 7.25 (t, 8, *m*-H)<br>7.46 (t, 8, *o*-H) | 38.5(d) 15.0(d) | 14.6 | 64 |
| **2b** | 1.76 (d, 3.3, $SCH_3$)[d)] | 7.12 (t, 8, *m*-H) | 37.6(d) 8.1(d) | 14.6 | 36 |
| **3a** | 2.67 (d, 12.8, $C\underline{H}^aH^bPh$)<br>4.66 (d, 12.8, $CH^a\underline{H}^bPh$) | 6.54 (t, 3.7, Bn–H), 7.19 (t, 7, *m*-H)<br>7.47 (t, 7.7, *o*-H) | 37.0(d) 8.3(d) | 15.5 | 62 |
| **3b** | 2.46 (d, 13.2, $C\underline{H}^aH^bPh$)<br>3.49 (d, 13.2, $CH^a\underline{H}^bPh$) | 6.76 (b, Bn-H), 7.11 (t, 7, *m*-H) | 41.1(d) 15.8(d) | 15.5 | 38 |
| **4a** | 4.88 (d, 16.2, $CH{=}CH^c\underline{H}^t$)<br>5.02 (d, 9.9, $CH{=}C\underline{H}^cH^t$)<br>5.15 (m, $C\underline{H}{=}CH_2$) | 7.20 (t, 7.4, *m*-H), 7.24 (t, 7, *m*-H) | 39.0(d) 15.3(d) | 15.5 | 68 |
| **4b** | 4.83 (d, 16, $CH{=}CH^c\underline{H}^t$)<br>4.92 (d, 10, $CH{=}C\underline{H}^cH^t$)<br>5.15 (m, $C\underline{H}{=}CH_2$) | 7.11 (t, 6.8, *m*-H) | 37.7(d) 8.7(d) | 13.3 | 32 |
| **5a** | 1.02 (d, 5.5, $CHC\underline{H}_3$)<br>1.18 (d, 2.6, $SCH_3$)<br>2.21 (t, 14, $SC\underline{H}^aH^b$)<br>2.46 (t, 14, $SCH^a\underline{H}^b$) | 7.09 (t, 6, *m*-H) | 38.1(d) 13.7(d) | 14.7 | 50 |
| **5b** | 1.08 (d, 5.9, $CHC\underline{H}_3$)<br>1.75 (d, 2.9, $SCH_3$) | | 36.7(d) 7.5(d) | 14.6 | 30 |
| **5c** | 0.98 (d, 6.2, $CHC\underline{H}_3$)<br>1.89 (d, 3.3, $SC\underline{H}_3$) | | 40.9(d) 14.9(d) | 14.7 | 12 |
| **5d** | 1.46 (d, 3.3, $SCH_3$) | | 41.3(d) 11.7(d) | 14.7 | 8 |
| **6**[e)] | 1.20 (d, 5, $SCH_3$) | −10.6 (ddd, 59.7, 36.7, 16.9, Ru$\underline{H}$) | 43.4(d) 29.8(dd)<br>36.8(d) | 44<br>14.7 | |
| **7**[e)] | 2.1 (m, $PC\underline{H}_2$)<br>2.2 (m, $PC\underline{H}_2$) | −5.87 (ddd, 115.7, 20.2, 16.8, RuH)<br>6.50 (t, 7, *p*-H), 6.80 (t, 7, *m*-H)<br>7.00 (d, 7, *o*-H) | 64.1(d) 42.0(dd)<br>36.0(d) | 292<br>18.9 | |

a) δ value from TMS in $CDCl_3$ at −50 °C for **2**—**5**. Signal shape, coupling constant (Hz), and assignment are given in parentheses. b) Protons which could not be assigned unambiguously are omitted. c) δ value in $CDCl_3$ from external 85% $H_3PO_4$. At −50 °C for **2**—**5**. d) As for the trimethylene protons, see the text. e) At room temperature.

bonded sulfur atom in **2**—**4** probably prevents the two $PPh_3$ ligands from lying trans to each other owing to steric repulsion.

In order to assign the phosphorus atoms and the trimethylene protons, $^1H^{31}P$-COSY and $^1H^1H$-COSY spectra of **2** were obtained as a representative. Phosphorus resonances at δ=38.5 and 37.6 correlate intensively with the S-methly protons, while those at

Table 2. $^{13}C\{^1H\}$ NMR Data of the Ruthenium(II) Complexes[a)]

| Complex | $Ru\underline{C}H_2$[b)] | $CH_2\underline{C}HY\underline{C}H_2S$ | Aryl moiety[b)] |  |  | C≡O | Others[d)] |
|---|---|---|---|---|---|---|---|
|  |  |  | *m*-C | *p*-C | *i*- or *o*-C[c)] |  |  |
| **2a** | — | 32.7, 42.2 | 127.4 (d, 7.8)<br>127.6 (d, 7.8) | 129.1<br>129.3 | 133.3 (d, 21)<br>133.8 (d, 23) | 204.9 (b) | 18.3 [$SCH_3$] |
| **2b** | — | 33.3 | 127.8 (d, 7.8) | 128.7 |  | 201.9 (b) | 18.3 [$SCH_3$] |
| **3a** | 33.7 (d, 49) | 32.8, 36.7 | 128.1 (d, 7.8) |  |  | 202.0 (b) | 38.0 [$\underline{C}H_2Ph$] |
| **3b** | — | 32.1, 36.5 | 127.8 (d, 7.8) |  |  | 204.2 (b) | 38.9 [$\underline{C}H_2Ph$] |
| **4a** | 32.7 (d, 60.6) | 32.6, 35.4 | 127.7 (b) | 129.2<br>129.4 | 135.1 (d, 27.4) | 203.9 (b) | 36.7 [$\underline{C}H_2CH=$]<br>119.3 [$CH_2\underline{C}H=$] |
| **4b** |  | 35.7 | 127.9 (b) | 128.8 | 153.3 (d, 24.4) | 201.7 (b) | 38.2 [$\underline{C}H_2CH=$]<br>117.8 [$CH_2\underline{C}H=$] |
| **5a** | 42.0 (d, 60) | 41.3, 45.9 |  | 129.3 |  | 204.2 (b) | 18.6 [$SCH_3$]<br>22.4 [$CH\underline{C}H_3$] |
| **5b** | 40.7 (d, 54) | 35.8, 46.1 |  | 129.0 |  | 204.1 (b) | 14.4 [$SCH_3$]<br>21.8 [$CH\underline{C}H_3$] |
| **5c** | 39.1 (d, 60) | 35.4, 49.2 |  | — |  | 202.0 (b) | 13.8 [$S\underline{C}H_3$]<br>21.4 [$CH\underline{C}H_3$] |
| **6**[e)] | — | — | 127.7 (d, 7.8)<br>127.9 (d, 7.8) | 129.5<br>129.7 | 133.6 (d, 40)<br>134.1 (d, 11.7)[f)]<br>134.2 (d, 11.8)[f)]<br>134.6 (d, 11.6)[f)] | 202.3 (t, 11)<br>203.2 (d, 15) | 27.0 [$SCH_3$] |

a) $\delta$ value from TMS in $CDCl_3$ at −50 °C, unless noted elsewhere. Singlet, unless noted. Other signal shape and coupling constant (Hz) are given in parentheses; d=doublet, t=triplet, and b=broad. b) Carbons which could not be assigned unambigously are omitted. c) Ipso-carbon, unless noted elsewhere. d) Assignment is bracketed. e) At room temperature. f) *o*-Carbon.

$\delta$=15.0 and 8.1 do not at all. Therefore, the phosphorus resonances at $\delta$=38.5 and 37.6 are ascribed to trans positions to the methythio groups in the two isomers of **2**. As the phosphorus resonance at $\delta$=15.0 correlates moderately with two broad proton signals at $\delta$=1.63 and 2.08, these two signals are assigned to ruthenium-bonded methylene protons of the major isomer of **2**. Furthermore, the signals at $\delta$=1.63 and 2.08 correlate with that at $\delta$=1.90 [overlapping with impurity siganl (THF)] (Fig. 1). In addition, the signal at $\delta$=2.08 has also correlations with that at $\delta$=1.74 [(overlapping with the doublet at $\delta$=1.76 ($SC\underline{H}_3$ of the minor isomer)]. Therefore, these two signals at $\delta$=1.90 and 1.74 are assignable to two protons of 2-methylene group. The signal at $\delta$=1.74 correlates intensively with a doublet $\delta$=2.29 ($J$=12 Hz) and a triplet at $\delta$=2.67 ($J$=12 Hz). These doublet and triplet are assignable to S-bonded methylene protons, taking account of these correlations and the comparatively low-field chemical shifts.

As for the minor isomer, the phosphorus atom at $\delta$=8.1 has moderate correlations with broad proton signals at $\delta$=1.53 and 2.09, which correlate intensively with each other and are assignable to the ruthenium-bonded methylene protons. A broad doublet at $\delta$=2.75 and a broad signal at $\delta$=2.20 correlate with each other and are ascribable to S-bonded methylene protons in consideration of the comparatively low-field chemical shifts. Signals at $\delta$=1.36 (overlapping partly with water signal) and 2.14 correlate with the signals at $\delta$=2.75 and 1.53, respectively, in addition to moderate correlation between each other, and are assignable to protons of 2-methylene group.

Methyl 2-methyl-2-propenyl sulfide reacted with **1** at 28 °C to afford $[Ru(CH_2CHMeCH_2SMe)Cl(CO)(PPh_3)_2]$ (**5**) in 53% yield. Its $^{31}P\{^1H\}$ NMR spectrum at −50 °C exhibited four sets of AB patterns (Table 1), implying that **5** consisted of four structural isomers at this temperature, owing to the structural isomerism at 2-carbon and the quench of the inversion of the methyl group upon the sulfur atom. The ratio of the four isomers was about 50 : 30 : 12 : 8. The carbons of the least isomer **5d** were not detected clearly. The IR spectrum of **5** showed a strong absorption band at 1908 $cm^{-1}$, ascribable to metal-bonded carbonyl group. Accordingly, the structural isomerism does not affect the stretching vibration frequency of the carbonyl group actually.

**Thermal Reaction of 2.** Upon heating at 67 °C for 6 h, **2** was converted into $[Ru_2Cl_2H(SMe)(CO)_2(PPh_3)_3]$ (**6**) evolving propylene. Similar C–S bond fission was reported with regard to reactions between allylic aryl sulfides and $[RhH(PPh_3)_4]$ or $[RuH_2(PPh_3)_4]$.[6)] However, no (phenylthio)ruthenium complex had been isolated from the reaction of $[RuH_2(PPh_3)_4]$ with allyl phenyl sulfide.[6)]

The $^1H$ NMR spectrum of **6** showed a doublet of doublet of doublet at $\delta$=−10.6, assignable unambiguously to bridging hydrido ligand. Two larger coupling constants [$^2J_{(HP)}$=59.7 and 36.7 Hz] were due to *trans*-located $PPh_3$ ligands, whereas the smallest one [$^2J_{(HP)}$=16.9 Hz] was to *cis*-situated phosphine. The S-bonded methyl protons resonated as a doublet at $\delta$=1.20,

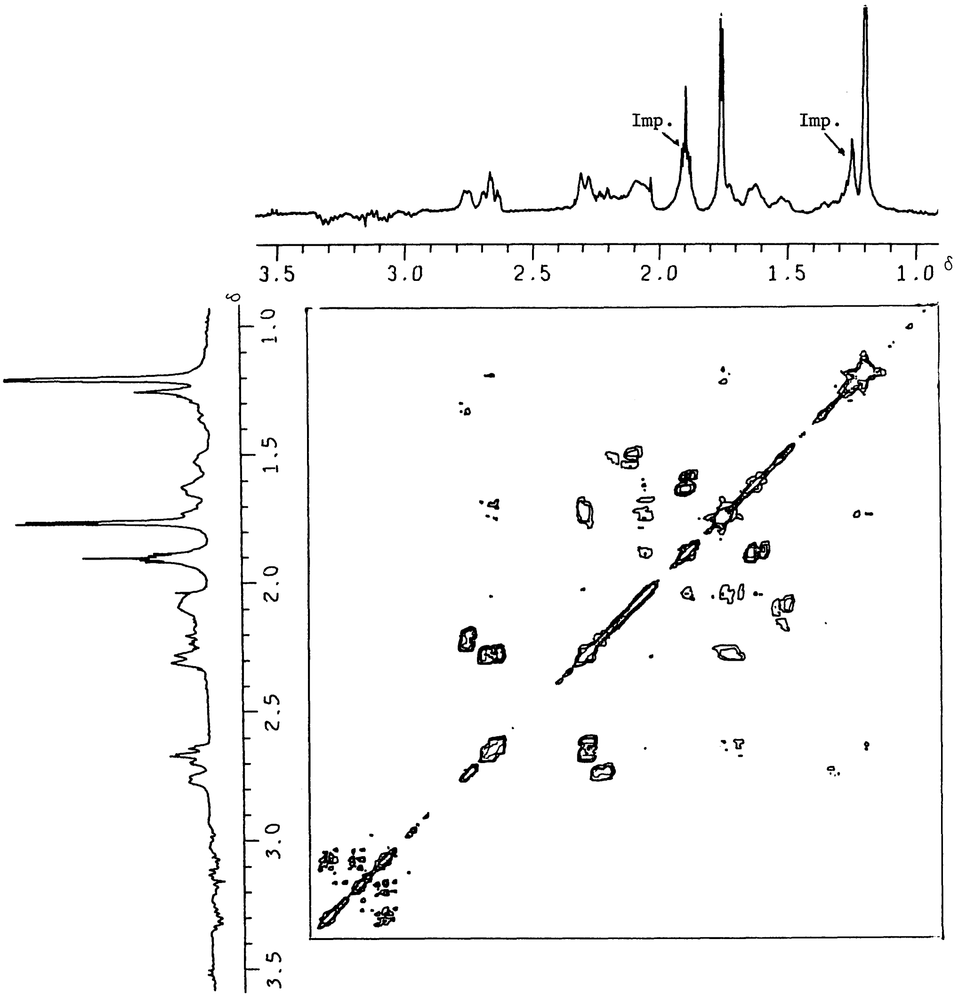

Fig. 1. $^1H^1H$-COSY spectrum of **2** in $CDCl_3$.

indicating *trans*-coordination of one $PPh_3$ ligand to the methythio group. Its $^{31}P\{^1H\}$ NMR spectrum exhibited two doublets at $\delta=43.4$ [$^4J_{(PP)}=44$ Hz] and 36.8 [$^2J_{(PP)}=14.7$ Hz] and one double doublet at $\delta=29.8$ (Table 1). As for these three non-equivalent phosphorus atoms, the smaller coupling constant was ascribed to two *cis*-coordinated phosphines. It is noted that the larger coupling constant was associated with a long range coupling through four bonds (P–Ru–H–Ru–P) between two phosphorus atoms coordinated to the different ruthenium atoms. In $^{13}C\{^1H\}$ NMR spectrum, two carbonyl carbons resonated as one doublet and one triplet (Table 2), supporting the above assignment. Therefore, **6** was assignable to one of two coordination position isomers, each of which had an asymmetric binuclear structure, as shown in Fig. 2. It is noteworthy that **6** involves a unique triply-bridged structure, consisting of three kings of bridging ligands, hydrido, methylthio, and chloro. A triply-bridged structure of a $(\mu\text{-}Cl)_3$ type was reported for many binuclear (tertiary phosphine)ruthenium (II) complexes.[8] Recently, Dev et al. prepared triply-thiolato-bridged binuclear ruthenium complexes $[Ru_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SAr)_3]^+$ [9] and $[Ru_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SR)_3]$ (R=$Pr^i$ and so on),[10] whereas a triply-mercapto-bridged structure was also reported for $[Ru_2(\mu\text{-}SH)_3(SH)(PMe_2Ph)_5]$.[11]

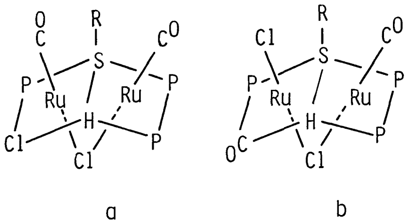

Fig. 2. Possible structures for **6**. P=$PPh_3$.

The FAB-mass spectrum of **6** showed two large sets near $m/z$=1129 and 1117 and two moderate ones near $m/z$=1164 and 902. Each set demonstrates a very complicated pattern, consisting of about eight signals, since each set corresponds to the ionic species containing

$\mathrm{Ru_2Cl_2S}$, $\mathrm{Ru_2ClS}$, or $\mathrm{Ru_2Cl_2}$ moiety and the ruthenium, chlorine, and sulfur atoms are composed of seven, two, and four stable isotopes, respectively.[12] The signal at $m/z$=1164 is ascribed to the most abundant species of the parent ions, and corresponds to the sum of $[^{102}\mathrm{Ru}_2{}^{35}\mathrm{Cl}_2\mathrm{H}(^{32}\mathrm{SCH}_3)(\mathrm{CO})_2(\mathrm{PPh}_3)_3]$, $[^{104}\mathrm{Ru}^{100}\mathrm{Ru}^{35}\mathrm{Cl}_2\mathrm{H}(^{32}\mathrm{SCH}_3)(\mathrm{CO})_2(\mathrm{PPh}_3)_3]$, $[^{102}\mathrm{Ru}^{100}\mathrm{Ru}^{35}\mathrm{Cl}^{37}\mathrm{ClH}(^{32}\mathrm{SCH}_3)(\mathrm{CO})_2(\mathrm{PPh}_3)_3]$, and so on. The other signals at $m/z$=1129, 1117, and 902 are assignable to $\mathrm{P}-{}^{35}\mathrm{Cl}$ (P=parent ion), $\mathrm{P}-{}^{32}\mathrm{SCH}_3$, and $\mathrm{P}-\mathrm{PPh}_3$, respectively. These data support the above formulation of **6**.

**Preparation of [RuClH(CO)(dppe)(PPh$_3$)] and Its Reaction with Allyl Methyl Sulfide.** Complex **1** reacted smoothly with 1,2-bis(diphenylphosphino)ethane (dppe) to give $[\mathrm{RuClH(CO)(deep)(PPh_3)}]$ (**7**). Its $^1$H NMR spectrum showed a doublet of doublet of doublet at $\delta=-5.87$, assigned to hydrido ligand. The large coupling constant [$^2J_{(\mathrm{HP})}$=115.7 Hz] is caused by *trans*-coordinated phosphine, whereas two small ones [$^2J_{(\mathrm{PH})}$=20.2 and 16.8 Hz] are due to two unequivalent phosphines, lying cis to the hydrido ligand. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **7** exhibited two doublets at $\delta$=36.0 and 64.1 and one double doublet at $\delta$=42.0. These data imply that **7** contains three unequivalent phosphine moieties, which are coordinated in a meridional form. It is noted that coupling constant between the two doublets at $\delta$=36.0 and 64.1 is too small to be detected at room temperatuure and even at −50 °C, although the two phosphorus atoms corresponding to the doublets are coordinated cis to each other. Accordingly, the dppe ligand replaced two PPh$_3$ ligands in **1**, leaving the other ligands unchanged to give **7** (Scheme 1).

Complex **7** did not react with allyl methyl sulfide in THF at 50 °C, but did in refluxing toluene for 15.5 h to give pale yellow precipitates, $[\mathrm{Ru_2Cl_2(SCH_3)_2(CO)_2(dppe)_2}]$ (**8**). Complex **7** is more sluggish toward alkyl allyl sulfide than **1**, probably because the four phenyl groups of dppe in **7** exert less steric effect toward the leaving PPh$_3$ ligand than the six phenyl groups of the two PPh$_3$ ligands in **1** do. The IR spectrum of **8** showed strong bands at 1950, 1480, and 1430 cm$^{-1}$, ascribable to $\nu$ (C≡O), $\nu$ (C=C in $\mathrm{C_6H_5}$) and $\nu$ (P-$\mathrm{C_6H_5}$), respectively. As **8** was not soluble in organic solvents, neither NMR spectrum nor molecular weight could not be obtained. Complex **8** was assigned to a binuclear structure bridged with two methylthio groups (Scheme 1), on the basis of the elemental analyses, the IR data, and the insolubility. A few coordination position isomers are possible for **8** owing to the relative positions of the carbonyl and chloro ligands.

## Experimental

The starting ruthenium complex **1**,[13] allyl methyl sulfide,[14] allyl benzyl sulfide,[15] and methyl 2-methyl-2-propenyl sulfide[16] were prepared according to literature methods. Diallyl sulfide was commercially available. General procedures were described previously.[4] Mass spectrum was recorded on a JEOL model JMS DX-303 spectrometer.

**Reaction of 1 with Allyl Methyl Sulfide.** A THF suspension (20 cm$^3$) containing 501 mg (0.53 mmol) of **1** and 228 mg (2.56 mmol) of allyl methyl sulfide was stirred at 25 °C for 5 h. The pink suspension changed to an orange solution gradually. The orange solution was concentrated to ca. 6 cm$^3$ under reduced pressure and diluted with hexane to afford pale yellow solid.

$[\mathrm{Ru(CH_2CH_2CH_2SMe)Cl(CO)(PPh_3)_2}]$ (**2**). Yield 53%, mp 149—150 °C, IR (KBr) 1920 (C≡O), 1480 ($\mathrm{C_6H_5}$), and 1425 cm$^{-1}$ (P-$\mathrm{C_6H_5}$). Found: C, 63.34; H, 5.26%. Calcd for $\mathrm{C_{41}H_{39}ClOP_2RuS}$: C, 63.27; H, 5.05%.

**Reaction of 1 with Allyl Benzyl Sulfide.** Complex **1** reacted with allyl benzyl sulfide at 10 °C for 10 h in analogous fashions to the case of **2** to give pale yellow solid.

$[\mathrm{Ru(CH_2CH_2CH_2SCH_2Ph)Cl(CO)(PPh_3)_2}]$ (**3**). Yield 69%, mp 146—150 °C, IR (KBr) 1920 (C≡O), 1475 ($\mathrm{C_6H_5}$), and 1425 cm$^{-1}$ (P-$\mathrm{C_6H_5}$). Found: C, 65.95; H, 5.81%. Calcd for $\mathrm{C_{47}H_{43}ClOP_2RuS}$: C, 66.07; H, 5.07%.

**Reaction of 1 with Diallyl Sulfide.** Complex **1** was treated with five times molar amounts of diallyl sulfide in THF at 10 °C for 8 h similarly to afford pale yellow solid.

$[\mathrm{Ru(CH_2CH_2CH_2SCH_2CH{=}CH_2)Cl(CO)(PPh_3)_2}]$ (**4**). Yield 75%, mp 124—126 °C, IR (KBr) 1915 (C≡O), 1480 ($\mathrm{C_6H_5}$), and 1430 cm$^{-1}$ (P-$\mathrm{C_6H_5}$). Found: C, 63.78; H, 5.64%. Calcd for $\mathrm{C_{43}H_{41}ClOP_2RuS}$: C, 64.21; H, 6.14%.

**Reaction of 1 with Methyl 2-Methyl-2-propenyl Sulfide.** Complex **1** reacted with methyl 2-methyl-2-propenyl sulfide at 28 °C in THF for 6 h to afford pale greenish yellow solid.

$[\mathrm{Ru(CH_2CHMeCH_2SMe)Cl(CO)(PPh_3)_2}]$ (**5**). Yield 46%, mp 169—172 °C, IR 1908 (C≡O), 1480 ($\mathrm{C_6H_5}$ ring), 1430 cm$^{-1}$ (P-$\mathrm{C_6H_5}$). Found: C, 63.96; H, 5.38%. Calcd for $\mathrm{C_{42}H_{41}ClOP_2RuS}$: C, 63.67; H, 5.22%.

**Thermal Reaction of 2.** A THF solution (20 cm$^3$) of **2** (218 mg) was refluxed for 18 h under nitrogen atmosphere. After the reaction mixture was evacuated under reduced pressure, the residue was chromatographed on a silica gel column. A colorless fraction, eluted with hexane–dichloromethane (1 : 1), afforded triphenylphosphine oxide. An orange fraction was eluted with dichloromethane and diluted with hexane to give orange solid.

$[\mathrm{Ru_2Cl_2H(SCH_3)(CO)_2(PPh_3)_3}]$ (**6**). Yield 32%, mp 147—150 °C, IR (KBr) 1950 (C≡O), 1585 (w, $\mathrm{C_6H_5}$), 1480 ($\mathrm{C_6H_5}$), 1432 (P-$\mathrm{C_6H_5}$), 1310 (w, $\mathrm{SCH_3}$), and 1090 cm$^{-1}$ (coordinated P-$\mathrm{C_6H_5}$). FAB-MS (3-nitrobenzyl alcohol as a matrix) $m/z$=1164 [P(parent ion), Int.=13], 1129 ($\mathrm{P}-{}^{35}\mathrm{Cl}$, Int.=100), 1117 ($\mathrm{P}-{}^{32}\mathrm{SCH}_3$, Int.=62), and 902 ($\mathrm{P}-\mathrm{PPh}_3$, Int.=17). Found: C, 55.74; H, 4.50%. Calcd for $\mathrm{C_{57}H_{49}Cl_2O_2P_3Ru_2S}$–$\mathrm{CH_2Cl_2}$: C 55.78; H, 4.12%.

**Reaction of 1 with 1,2-Bis(diphenyphosphino)ethane.** A benzene suspension (50 cm$^3$) containing 0.84 mmol of **1** and 0.92 mmol of 1,2-bis(diphenylphosphino)ethane (dppe) was stirred under nitrogen atmosphere at room temperature for 24 h. The reaction mixture was concentrated under reduced pressure and diluted with hexane to afford greyish white solid.

$[\mathrm{RuClH(CO)(dppe)(PPh_3)}]$ (**7**). Yield 97%, mp 243—246 °C, IR (KBr) 1925 (C≡O), 1485 ($\mathrm{C_6H_5}$), 1435 (P-$\mathrm{C_6H_5}$), and 1095 cm$^{-1}$ (coordinated P-$\mathrm{C_6H_5}$). Found: C, 65.49; H, 5.05%. Calcd for $\mathrm{C_{45}H_{40}ClOP_3Ru}$: C, 65.42; H, 4.88%.

**Reaction of 7 with Allyl Methyl Sulfide.** When complex **7** (0.48 mmol) was treated with an excess amount (2.42 mmol) of allyl methyl sulfide in refluxing toluene for 15.5 h, pale yellow precipitates were formed. The precipitates were collected, washed with hexane, and dried in vacuo to give pale yellow solid.

$[Ru_2Cl_2(\mu\text{-}SCH_3)_2(CO)_2(dppe)_2]$ (**8**). Yield 99%, IR (KBr) 1950 (C≡O), 1480 ($C_6H_5$), 1430 (P-$C_6H_5$), and 1090 $cm^{-1}$ (coordinated P-$C_6H_5$). Found: C, 54.65; H, 4.51%. Calcd for $C_{56}H_{54}Cl_2O_2P_4Ru_2S_2$: C, 55.13; H, 4.46%

This work was supported by Grant-in-Aid for Scientific Research Nos. 62215029 and 63106006 from the Ministry of Education, Science and Culture.

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