tert-butylacetylide precursor of course indicates that structure II and not I is present, and therefore reaction with CO is readily interpreted as occurring in a manner exactly analogous to that in the chloro-bridged analogue; CO coordination is accompanied by the formation of a Rh–Rh bond. Although it is possible that CO coordination could be accomplished by a change in the acetylide bonding mode, we feel that this is unlikely in the present series of compounds. Not only would the above mentioned unfavorable contacts between the bridging CO and acetylide group result, but also the spectroscopic parameters[29] for the CO adducts agree very well with those of the analogous chloro-bridged species,[30] suggesting similar structure for these complexes.

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Registry No. $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]\cdot 0.866CH_2CL_2$, 95217-03-1; $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]$, 94294-51-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, the derived hydrogen positions, and the observed and calculated structure amplitudes (22 pages). Ordering information is given on any current masthead page.

(28) Without a metal–metal bond the carbon atoms of the bridging carbonyl and acetylide groups can be viewed as sp^2 hybridized and come into rather close contact. For a discussion of insertions into metal–metal bonds see: Cowie, M.; Dickson, R. S.; Hames, B. W. *Organometallics* **1984**, *3*, 1879.

(29) For the complexes $[Rh_2(CO)_2(\mu\text{-}C_2R)(\mu\text{-}CO)(DPM)_2]^+$ (R = H, Ph) the carbonyl stretches are at 1987, 1973, and 1856 cm^{-1} and at 1988, 1969, and 1872 cm^{-1}, respectively.

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Cleavage of C–S Bond in Allylic Aryl Sulfides Promoted by Rhodium Hydride Complex: Reaction Mechanisms of Allyl–Sulfur Bond Fission†

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Reactions of allylic aryl sulfides with $RhH(PPh_3)_4$ cause cleavage of allylic sulfur bond to afford rhodium thiolato complexes $[Rh(\mu\text{-}SAr)(PPh_3)_2]_2$ and olefins under mild conditions. Distributions of olefinic products in the reactions of sulfides having alkyl substituents on the allyl part such as 3-(phenylthio)-1-butene and 1-(phenylthio)-2-butene indicate that selective rearrangement of C═C bond occurs. The reaction of 3-(phenylthio)propene with $RhD(P(C_6D_5)_3)_4$ gives propylene as a mixture of C_3H_6, C_3H_5D, $C_3H_4D_2$, and $C_3H_3D_3$ with recovery of partly deuterated 3-(phenylthio)propene, suggesting hydrogen exchange between 3-(phenylthio)propene and rhodium hydride complex prior to the C–S bond cleavage. New rhodium thiolato complexes obtained from these reactions are characterized by IR and/or NMR spectroscopy, elemental analysis, and their chemical reactions.

Introduction

Recently, various synthetic methods utilizing allyl–halogen, allyl–oxygen, and allyl–sulfur bond cleavage have been developed and successfully employed in synthetic organic chemistry.[1] Palladium and nickel complex catalyzed cross-coupling reactions of allylic electrophiles with nucleophilic reagents also are of interest.[2–6] In most of these reactions π-allyl complex intermediates are believed to be formed by direct bond cleavage induced by zerovalent complexes. However, reactions of allylic electrophiles with transition-metal complexes have been studied mainly with nickel and palladium complexes. Previous studies of our group revealed that reaction features of allylic carboxylates and allylic carbonates with group 8–10 metal hydrides[7] differ distinctly from those involving direct cleavage of allyl–oxygen bond induced by zerovalent nickel and palladium complexes.[8]

We have communicated in a preliminary note[9] that cleavage of the allyl–sulfur bond in allylic aryl sulfides

†The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

(1) (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. (b) Trost, B. M.; Keinan, E. *J. Am. Chem. Soc.* **1978**, *100*, 7780. (c) Atkins, K. E.; Walker, W. E.; Manyik, R. M. *Tetrahedron Lett.* **1970**, 3821. (d) Fiaud, J. C.; deGournay, H.; Larcheveque, M.; Kagan, H. B. *J. Organomet. Chem.* **1978**, *154*, 175. (e) Balavoine, G.; Bram, G.; Guibe, F. *Nouv. J. Chim.* **1978**, *2*, 207. (f) Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* **1977**, *139*, C45. (g) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* **1979**, 613. (h) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Ibid.* **1978**, 2075. (i) Tsuda, T.; Chujo, Y.; Nishi, S.; Tawara, K.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 6381. (j) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 1793. (k) Shimizu, I.; Minami, I.; Tsuji, J. *Ibid.* **1983**, *24*, 1797. (l) Hutchins, R. O.; Learn, K.; Fulton, R. P. *Tetrahedron Lett.* **1980**, *21*, 27. (m) Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4382.
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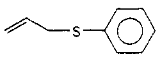
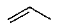
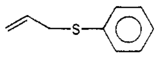
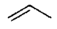
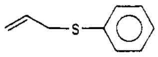
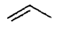
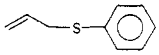
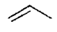
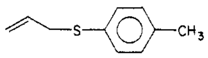
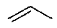
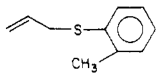
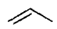
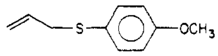
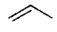
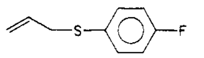
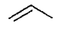
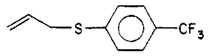
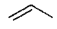
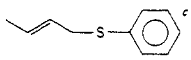
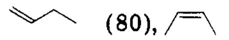
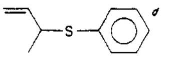
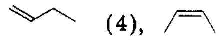
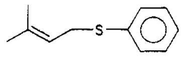
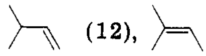
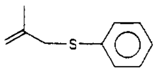
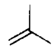
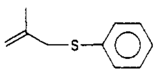
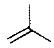
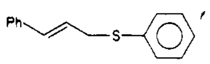
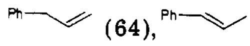
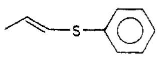
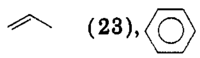
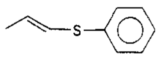
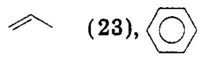
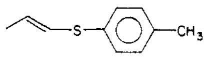
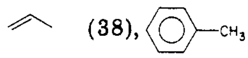
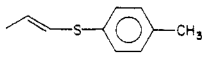
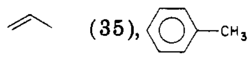
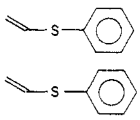
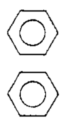
(8) (a) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 6863. (b) Yamamoto, T.; Saito, O.; Yamamoto, A. *Ibid.* **1981**, *103*, 5600. (c) Yamamoto, T.; Akimoto, M.; Yamamoto, A. *Chem. Lett.* **1983**, 1725.

Table I. Reaction of Sulfide with Metal Hydride Complexes[a]

run	complex	react time, h	sulfide	product (yield, %): olefin (and other products)[b]	product (yield, %): complex
1	$RhH(PPh_3)_4$	3		 (96)	1 (91)
2	$RhH(CO)(PPh_3)_3$	4		 (83)	
3	$CoH(N_2)(PPh_3)_3$	4		 (42)	
4	$RuH_2(PPh_3)_4$	22		 (23)	
5	$RhH(PPh_3)_4$	5		 (100)	2 (98)
6	$RhH(PPh_3)_4$	5		 (100)	
7	$RhH(PPh_3)_4$	2		 (96)	3 (91)
8	$RhH(PPh_3)_4$	2		 (92)	4 (94)
9	$RhH(PPh_3)_4$	2		 (93)	5 (73)
10	$RhH(PPh_3)_4$	2	 [c]	 (15, *E/Z* = 13/87)	1 (100)
11	$RhH(PPh_3)_4$	2	 [d]	 (78, *E/Z* = 21/79)	1 (95)
12	$RhH(PPh_3)_4$	50		 (62)	
13	$RhH(PPh_3)_4$	50		 (3)	
14[e]	$RhH(PPh_3)_4$	5		 (12)	
15	$RhH(PPh_3)_4$	3	 [f]	 (21, *E/Z* = 100/0)	1 (83)
16	$RhH(PPh_3)_4$	30		 (80)	
17[g]	$RhH(PPh_3)_4$	24		 (87)	
18	$RhH(PPh_3)_4$	30		 (46)	
19[g]	$RhH(PPh_3)_4$	24		 (58)	
20	$RhH(PPh_3)_4$	24		C_2H_4 (16),  (70)	
21[g]	$RhH(PPh_3)_4$	24		C_2H_4 (22), (77)	

[a] Reactions in toluene at room temperature. Sulfide/hydrido complex = 1/1. [b] GLC yields based on complex. [c] *E/Z* = 76/24. A small amount (<4%) of 3-(phenylthio)-1-butene is contained. [d] A small amount (<6%) of 1-(phenylthio)-2-butene is contained. [e] Reaction at 70 °C. [f] *E/Z* = 100/0. [g] Sulfide/rhodium = 3/1.

promoted by $RhH(PPh_3)_4$ proceeds in a manner distinctly different from reactions of allylic chalcogen compounds with Pd(0) complexes.[8c] Such metal-promoted C–S bond fission has been of recent interest with regard to hydrodesulfurization using heterogeneous catalysis.[10] We now report the full details of the reactions and the mechanistic study.

(9) Osakada, K.; Matsumoto, K.; Yamamoto, T.; Yamamoto, A. *Chem. Ind. (London)* **1984**, 634.
(10) Lesch, D. A.; Richardson, J. W.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901.

Results and Discussion

Reactions of $RhH(PPh_3)_4$ with Allylic Aryl Sulfides. Reactions of 3-(phenylthio)propene with transition-metal hydride complexes such as $RhH(PPh_3)_4$, $RhH(CO)(PPh_3)_3$, $CoH(N_2)(PPh_3)_3$, and $RuH_2(PPh_3)_4$ give propylene (eq 1) which is formed by coupling of the allyl group in the sulfide and the hydride ligand (Table I).

$$CH_2{=}CHCH_2SC_6H_4R + RhH(PPh_3)_4 \xrightarrow{-2PPh_3} C_3H_6 + {}^1/_2[Rh(\mu\text{-}SC_6H_4R)(PPh_3)_2]_2 \quad (1)$$

R = H, *p*-CH_3, *o*-CH_3, *p*-OCH_3, *p*-F, and *p*-CF_3

Table II. NMR Data of the Complexes

complex	$^{1}H^{a}$	$^{31}P\{^{1}H\}^{b}$	$^{19}F^{c}$
$[Rh(\mu\text{-}SC_6H_4OCH_3)(PPh_3)_2]_2$ (3)	3.3 (s, 6 H, OCH_3) 6.3, 7.7 (ABq, 8 H, C_6H_4)	48.5 (d, $J_{Rh\text{-}P}$ = 170 Hz)	
$[Rh(\mu\text{-}SC_6H_4F)(PPh_3)_2]_2$ (4)	6.3, 7.1 (ABq, 8 H, C_6H_4)	48.6 (d, $J_{Rh\text{-}P}$ = 170 Hz)	−44.5 (s)
$[Rh(\mu\text{-}SC_6H_4CF_3)(PPh_3)_2]_2$ (5)		47.9 (d, $J_{Rh\text{-}P}$ = 169 Hz)	12.8 (s)
$[Rh(\mu\text{-}SC_6H_5)(CO)(PPh_3)]_2$ [d]			
6a (cis)		43.5 (d, $J_{Rh\text{-}P}$ = 155 Hz)	
6b (trans)		45.2 (d, $J_{Rh\text{-}P}$ = 158 Hz)	
$[Rh(\mu\text{-}SC_6H_4CH_3)(CO)(PPh_3)]_2$ [d]			
7a (cis)	2.15 (s, 3 H, CH_3) 2.23 (s, 3 H, CH_3) 6.9, 7.1 (ABq, 4 H, C_6H_4) 7.6, 8.5 (ABq, 4 H, C_6H_4)	43.3 (d, $J_{Rh\text{-}P}$ = 155 Hz)	
7b (trans)	2.1 (s, 6 H, CH_3) 6.7, 7.8 (ABq, 8 H, C_6H_4)	45.2 (d, $J_{Rh\text{-}P}$ = 157 Hz)	
$[Rh(\mu\text{-}SC_6H_4OCH_3)(CO)(PPh_3)_2]_2$ [d]			
8a (cis)	3.1 (s, 3 H, OCH_3) 3.2 (s, 3 H, OCH_3) 6.5, 6.6 (ABq, 4 H, C_6H_4) 7.4, 8.3 (ABq, 4 H, C_6H_4)	43.2 (d, $J_{Rh\text{-}P}$ = 157 Hz)	
8b (trans)	3.24 (s, 6 H, OCH_3) 6.2, 7.1 (ABq, 8 H, C_6H_4)	45.2 (d, $J_{Rh\text{-}P}$ = 158 Hz)	

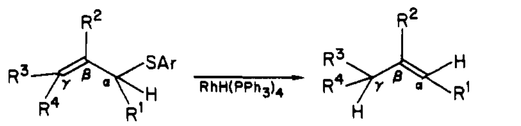
[a] 400 MHz in C_6D_6; δ. [b] 40 MHz in C_6D_6; parts per million downfield from external PPh_3. [c] 94 MHz in C_6D_6, parts per million downfield from external CF_3COOH. [d] A mixture of cis and trans isomers was measured.

$RhH(PPh_3)_4$ shows the highest reactivity and gives almost a quantitative amount of propylene (Table I, run 1). $RuH_2(PPh_3)_4$ is much less reactive, and considerable amounts of both 3-(phenylthio)propene and $RuH_2(PPh_3)_4$ are recovered unreacted from the reaction mixture even after 22 h. In the case of $CoH(N_2)(PPh_3)_3$, the propylene formed reacts further with 3-(phenylthio)propene to give the addition product $C_6H_{11}SPh$ (mixture of isomers).

Several other allyl aryl sulfides ($CH_2{=}CHCH_2SC_6H_4R$, R = p-CH_3, o-CH_3, p-OCH_3, p-F, and p-CF_3) undergo similar C–S bond cleavage reactions with $RhH(PPh_3)_4$ to give very high yields of propylene accompanied by formation of complexes formulated as $[Rh(\mu\text{-}SC_6H_4R)(PPh_3)_2]_2$. Bond cleavage between the aryl group and sulfur atom does not occur as judged by the absence of corresponding aromatic compounds in the reaction mixture.

The use of other allylic phenyl sulfides such as 1-(phenylthio)-2-butene and 3-(phenylthio)-1-butene causes evolution of the corresponding olefins with formation of the complex $[Rh(\mu\text{-}SPh)(PPh_3)_2]_2$ (1). Yields of olefins are strongly influenced by the steric factors in the allylic part of the sulfides. 3-Methyl-(1-phenylthio)-2-butene, having a trisubstituted C=C bond, requires much longer reaction time than other substrates (Table I, run 12). 2-Methyl-(3-phenylthio)propene with a methyl group at β-position in the sulfide scarcely reacts with $RhH(PPh_3)_4$ at room temperature (Table I, run 13).

In connection with the mechanism of the C–S bond cleavage it is of interest that the reaction of 1-(phenylthio)-2-butene with $RhH(PPh_3)_4$ gives 1-butene as the main olefin product (eq 2) whereas the reaction of 3-(phenylthio)-1-butene gives 2-butene predominantly (Table I, runs 10 and 11). In runs 12 and 15 (Table I), initially



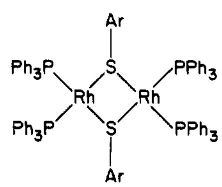
(2)

formed terminal olefins are gradually isomerized to the thermodynamically more stable internal olefins promoted by intact $RhH(PPh_3)_4$ as proved by periodic analysis of the olefin products in the reaction mixtures. All these results on the distribution of isomers in olefin products indicate clearly that selective bond rearrangement of the C=C double bond occurs in this reaction and that the new C=C double bond is formed between the α- and β-carbons (eq 2).

Vinyl aryl sulfides (e.g., 1-(phenylthio)propene, 1-(p-tolylthio)propene, and (phenylthio)ethene) undergo a different type of C–S bond cleavage promoted by $RhH(PPh_3)_4$. The main product of the reaction is benzene (or toluene) derived from scission of the aryl–sulfur bond. The yield of evolved propene (or ethene) is lower than that of benzene (or toluene) in each reaction.

Characterization and Properties of Rhodium Thiolato Complexes. As described above, dinuclear rhodium complexes $[Rh(\mu\text{-}SC_6H_4R)(PPh_3)_2]_2$ (**1**, R = H; **2**, R = p-CH_3; **3**, R = p-OCH_3; **4**, R = p-F; **5**, R = p-CF_3) are obtained from the reaction of allylic aryl sulfides with $RhH(PPh_3)_4$. Similar thiolato-bridged rhodium complexes with a structure of $[Rh(\mu\text{-}SR)(P(OR')_3)_2]_2$ (R = t-C_4H_9, C_6Cl_5; R′ = CH_3, C_6H_5) have been prepared from $P(OR')_3$ and $[Rh(\mu\text{-}SR)(CO)_2]_2$.[11] Structures of complexes **1**–**5** were confirmed by means of IR and/or NMR spectroscopy (Table II) and elemental analysis (Table III) as well as chemical reactions.

Although complexes **1** and **2** are not soluble in organic solvents, complexes **3**–**5** are amenable to NMR study. Complex **3** shows only one doublet in its $^{31}P\{^{1}H\}$ NMR spectrum and a single peak at δ 3.3 assigned to the methoxy hydrogen in its ^{1}H NMR spectrum. These NMR data and the molecular weights (Table III) are compatible with the dinuclear structure with two bridging thiolato ligands. A similar dinuclear structure has been proposed for $[Rh(\mu\text{-}SR)(P(OR')_3)_2]_2$. The ^{1}H, $^{31}P\{^{1}H\}$, and ^{19}F NMR data of **4** and **5** support a similar dinuclear structures (Table II).



(11) (a) Kemmit, R. D. W.; Rimmer, G. D. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3155. (b) Kalck, P.; Poilblanc, R.; Martin, R.-P.; Rovera, A.; Gaset, A. *J. Organomet. Chem.* **1980**, *195*, C9.

Table III. Melting Points, Analytical Data, and Molecular Weights of the Complexes

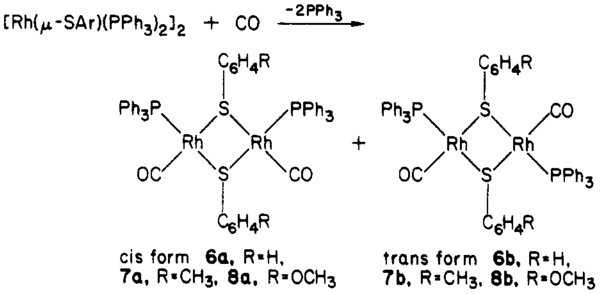
complex	mp, °C dec[a]	anal. found (calcd)			
		C	H	S	M_r (calcd)[b]
1	215	68.9 (68.5)	4.8 (4.8)	4.0 (4.3)	
2	210	68.6 (68.8)	5.0 (5.0)	4.1 (4.3)	
3	203	67.4 (67.4)	5.1 (4.9)	4.2 (4.2)	1400 (1533)
4	195	67.2 (66.9)	4.7 (4.5)		
5	169	64.3 (64.2)	4.1 (4.3)		
6a,b[c]		60.5 (59.8)	4.0 (4.0)	6.1 (6.4)	830 (1004)
7a,b[c]		61.1 (60.5)	4.4 (4.3)	6.2 (6.2)	790 (1030)
8a,b[c]		58.8 (58.7)	4.1 (4.2)	5.6 (6.0)	

[a] In vacuo. Uncorrected. [b] Measured by lowering of freezing point of benzene solution (10–20 mg/mL). [c] Mixture of cis and trans isomers.

Although the very low solubilities of complexes **1** and **2** do not allow measurements of NMR spectra and molecular weights, the IR spectra, chemical reactions, and elemental analyses support structures similar to **3**, **4**, and **5**. Reactions of CH_3I and C_6H_5I with **1** give (methylthio)benzene and diphenyl sulfide, respectively, in good yields. Complex **1** can be prepared independently from the reaction of equimolar PhSH or half-molar PhSSPh with $RhH(PPh_3)_4$ (eq 3), which is accompanied by evolution of H_2 (89% and 53%, respectively).

$$RhH(PPh_3)_4 + PhSH\ (\text{or } {}^1/_2\ PhSSPh) \xrightarrow{-2PPh_3} {}^1/_2\ [Rh(\mu\text{-}SPh)(PPh_3)_2]_2 + H_2\ (\text{or } {}^1/_2\ H_2) \quad (3)$$

Reactions of **1**, **2**, and **3** with CO readily give the corresponding rhodium complexes $[Rh(\mu\text{-}SAr)(CO)(PPh_3)]_2$ as mixtures of trans and cis isomers (eq 4).[12] The $^{31}P\{^1H\}$ NMR spectrum of the product of the reaction of **2** with CO shows two doublets of unequal intensities, suggesting that the product is a mixture of cis and trans isomers **7a** and **7b**.



(4)

The appearance of two CH_3 signals of equal intensity for **7a** and one CH_3 signal for **7b** in the ^1H NMR spectra also supports the structures above. The relative peak areas of the CH_3 signals in the ^1H NMR spectrum indicate that cis isomer **7a** exists as the major species in solution (ca. 88:12 at 35 °C).

Similar dinuclear rhodium complexes with bridged thiolato ligands $[Rh(\mu\text{-}SR)(CO)L]_2$ (R = $t\text{-}C_4H_9$, C_6Cl_5; L = PMe_3, $P(OMe)_3$, $P(NMe)_3$) have been prepared by reaction of LiSR with $[Rh(\mu\text{-}Cl)(CO)L]_2$ or by decarbonylation of $[Rh(\mu\text{-}SR)(CO)_2L]_2$.[12] A previous study of the detailed structure of these compounds revealed the presence of trans and cis isomers in some cases. $[Rh(\mu\text{-}SPh)(CO)(PMe_3)]_2$ is reportedly a mixture of trans and cis isomers (40:60) in CH_2Cl_2 solution, although only the cis isomer exists in cyclohexane.[13b] The ratio of **7a** and **7b** determined by $^{31}P\{^1H\}$ NMR does not change before and after repeated recrystallization, indicating attainment of rapid equilibration in solution. The temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum of the mixture in toluene in the range of −50 to +65 °C shows an increase in **7b** on raising the temperature, and a linear relationship exists between logarithm of the ratio of **7a** to **7b** and the reciprocal of the temperature as shown in Figure 1. From the data, thermodynamic parameters for **7a** ⇄ **7b** are calculated as $\Delta H° = 9.5$ kJ mol^{-1}, $\Delta S° = 13$ J mol^{-1} deg^{-1}, and $\Delta G° = 6.0$ kJ mol^{-1} at 273 K.

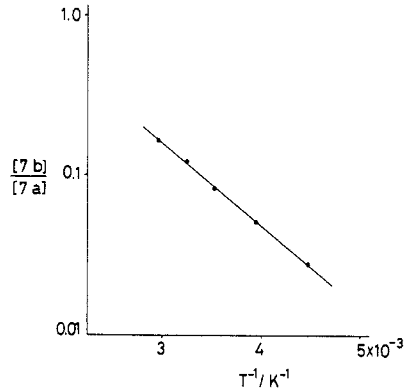


Figure 1. Temperature dependence of equilibrium constant for **7a** ⇄ **7b**.

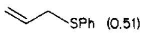
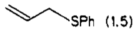
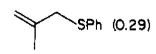
Complexes **6a** and **6b** and **8a** and **8b**, obtained from reactions of CO with **1** and **3**, respectively, exist as trans and cis isomer mixtures as proved by the NMR spectra similarly to **7a** and **7b**.

Reaction Mechanism for the Allyl–Sulfur Bond Cleavage Promoted by $RhH(PPh_3)_4$. Several processes can lead to the cleavage of the allyl–sulfur bond in the reaction of allylic aryl sulfides with the rhodium hydride complex. These are (i) direct cleavage of the allyl–sulfur bond to form a σ- or a π-allyl rhodium complex, (ii) isomerization of the allylic sulfide to a vinylic sulfide, followed by direct vinyl–sulfur cleavage, (iii) an S_N2' mechanism involving attack of the hydride ligand on the γ-carbon in the allylic group with concomitant transfer of the thiophenolato group to the metal, and (iv) insertion of the C=C double bond into the Rh–H bond to give an alkylrhodium species and subsequent abstraction of the thiophenolato group at the β-position by rhodium.

Mechanism i is operative in the reactions of Pd(0) or Ni(0) complexes with allylic esters and ethers[8] but is incompatible with the distribution of olefins observed in the present work. For example, according to the direct cleavage mechanism, 2-butene should be the main product

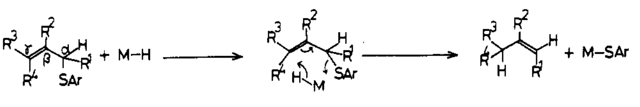
(12) The cis trans terminology here refers to coordination site of the two CO ligands with regards to the core $[Rh_2(SR)_2]$. See ref 13.
(13) (a) Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1975**, *11*, 2779. (b) Bonnet, J. J.; Kalck, P.; Poilblanc, R. *Ibid.* **1977**, *16*, 1514.
(14) Suzuki, H.; Koyama, Y.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1979**, *16*, 1415.
(15) (a) Dewolfe, R. H.; Young, W. G. *Chem. Rev.* **1956**, *56*, 769. (b) Young, W. G.; Clement, R. A.; Shih, C. *J. Am. Chem. Soc.* **1955**, *77*, 3061. (c) Stork, G.; White, W. N. *Ibid.* **1956**, *78*, 4604.

Table IV. Deuterium Incorporation into the Products in the Reaction of Phenyl Allylic Sulfides with $[RhD(P(C_6D_5)_3)_4]^a$

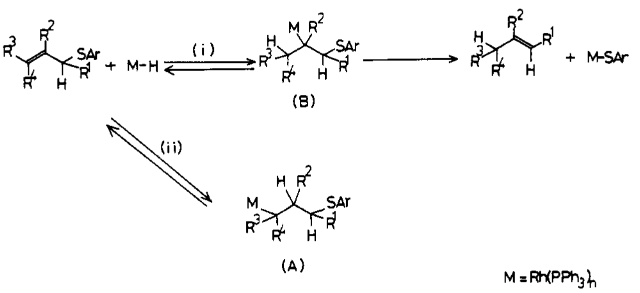
run	sulfide (mmol)	$[RhD(P(C_6D_5)_3)_4]$, mmol	products: olefin (mmol)	products: recovered sulfide	products: H/(H + D) in recovered PPh_3,[b] %
1		0.17	propylene (0.16) $d_0/d_1/d_2/d_3$[c] = 33/57/9/1	d_0/d_1[c] = 90/10	1.8
2		0.15	propylene (0.13) $d_0/d_1/d_2/d_3$[c] = 31/62/7/0	d_0/d_1[c] = 96/4	2.7[d]
3		0.10	2-methylpropene[e] (trace)	$d_0/d_1/d_2$ = 72/24/4	e

[a] See Experimental Section as to the measurement of deuterium content. [b] The molar ratio of H atoms incorporated into PPh_3 to the sum of H and D atoms of PPh_3. [c] Symbol "d_n" represents the molecule containing *n* deuterium atoms. [d] Complete removal of allyl phenyl sulfone from the sample was unsuccesful. [e] The ratio of ¹H and ²H was not measured.

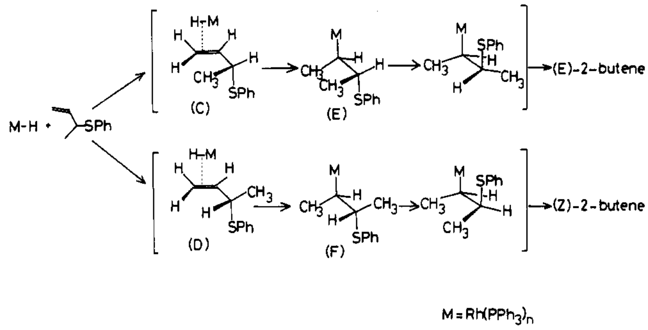
Scheme I



Scheme II



Scheme III



in run 10 and 1-butene should be the main product in run 11 (Table I). Furthermore, if π-allyl intermediates were involved, runs 10 and 11 would both give the same product, which was not observed.

The second possible mechanism involves Rh-catalyzed double-bond migration followed by cleavage of the vinylic sulfur bond thus formed. However, this mechanism is inconsistent with the observation that aryl–sulfur bonds are more readily cleaved than vinyl–sulfur bonds (runs 16–21).

The distribution of the olefinic products can be explained with either the S_N2' mechanism, in which the hydride ligand attacks the γ-carbon in the allylic group as shown in Scheme I, or the last mechanism involving C=C double bond insertion into the Rh-H bond followed by the elimination of rhodium and the thiolato ligand (Scheme II). The insertion-elimination mechanism seems more favorable on the basis of the following experimental evidence. In reactions of allylic phenyl sulfides with $RhH(PPh_3)_4$ 2-methyl(3-phenylthio)propene (run 13) is much less reactive than 3-methyl(1-phenylthio)-2-butene (run 12). The results indicate a greater steric effect of the CH_3 group at the β-carbon (see Schemes I and II) than the CH_3 group at the γ-carbon on the rate of the reaction, in accordance with Scheme II.

Further support for the insertion–elimination mechanism is available from studies of the reaction of $RhD(P(C_6D_5)_3)_4$ and excess 3-(phenylthio)propene. The propylene produced in the reaction was composed of C_3H_6, C_3H_5D, $C_3H_4D_2$, and $C_3H_3D_3$ as shown in Table IV. No propylene containing more than four deuteriums was detected. Recovered 3-(phenylthio)propene also contained deuterium derived from the rhodium complex. This result suggests that 3-(phenylthio)propene undergoes an H—D exchange reaction by repeated C=C insertion into Rh—D bond followed by β-hydrogen elimination to regenerate the sulfide prior to the C—S bond cleavage as depicted in paths i and ii in Scheme II. Ortho metalation of PPh_3[16] concomitantly occurring with the insertion–elimination process causes ¹H incorporation into the deuterated PPh_3 ligands as indicated in Table IV. The total amount of deuterium atoms contained in the propylene and the recovered 3-(phenylthio)propene agreed with that of ¹H atoms incorporated into PPh_3 ligands (Table IV, run 1). Thus the hydrogen exchange process is considered to be taking place prior to the irreversible rate-determining C–S bond cleavage process. In the reaction of 2-methyl(3-phenylthio)propane with $RhD(P(C_6D_5)_3)_4$ only a trace amount of 2-methylpropene was generated in the reaction at room temperature for 1 day but the sulfide recovered was labeled with deuterium.

According to the mechanism in Scheme II the dominance of (*Z*)-2-butene over *E* isomer in the olefin products in run 11 (Table I) is explained reasonably. Scheme III shows stereochemistry of the reaction intermediates. The steric repulsion between the methyl and vinyl groups in C and D indicates that D is more stable than C. Cis insertion in D leads to the formation of F from which MSPh is eliminated after rotation about the C–C bond, thus giving (*Z*)-2-butene as the major product.

In the reaction of vinylic aryl sulfides with $RhH(PPh_3)_4$, the aromatic hydrocarbon is obtained in a higher yield than the olefin, which is distinct from the reaction of allylic aryl sulfides. This difference of reactivity between allylic and vinylic sulfides may be attributed to the polarization of C=C bond in the vinylic aryl sulfides in which olefinic C=C bond has a nucleophilic nature like those of enamines or vinyl ethers. Such a character of C=C bond of the

(16) (a) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (c) Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235.

vinylic aryl sulfides may suppress the formation of alkyl intermediate A and cause another type of reaction with $RhH(PPh_3)_4$.

Experimental Section

General Procedures. Materials and Methods. All the reactions and manipulations of the complexes were carried out under nitrogen or under vacuum. Infrared spectra were recorded on a Hitachi 295 infrared spectrophotometer. NMR spectra were measured on JNM-PS-100, JNM-FX-100, and JNM-400-GX spectrometers. Elemental analysis was performed by Mr. T. Saito with Yanagimoto CHN Autocorder Type MT2 or performed at Sagami Chemical Research Center. GC–MS spectra were measured by a Hitachi M-80 mass spectrometer.

The preparation of allylic aryl sulfides and vinylic aryl sulfides was performed according to already reported procedures.[17] $RhH(PPh_3)_4$,[18] $RhH(CO)(PPh_3)_3$,[19] $CoH(N_2)(PPh_3)_3$,[20] and $RuH_2(PPh_3)_4$[21] were prepared according to the literature. $RhD(P(C_6D_5)_3)_4$ was prepared from $RhCl_3 \cdot 3H_2O$, $P(C_6D_5)_3$,[22] and $NaBD_4$ in EtOD, similar to the preparation of $RhH(PPh_3)_4$.

Reactions of Allylic Aryl Sulfides with $RhH(PPh_3)_4$. (a) 3-(Phenylthio)propene, 3-(*p*-Tolylthio)propene, and 3-(*o*-Tolylthio)propene. 3-(Phenylthio)propene (110 mg, 0.73 mmol) was added to a Schlenk tube containing 830 mg of $RhH(PPh_3)_4$ (0.72 mmol) and toluene (15 mL). After evacuation of the tube, the mixture was stirred at room temperature. Evolution of 0.69 mmol (96%/Rh) of propylene in the gas phase was observed as measured by means of GLC. The orange-red solid $[Rh(\mu\text{-}SPh)(PPh_3)_2]_2$ (1; 480 mg, 91%/Rh), which had precipitated from the reaction mixture, was filtered, washed with Et_2O several times, and dried in vacuo. Reactions of 3-(*p*-tolylthio)propene and 3-(*o*-tolylthio)propene with $RhH(PPh_3)_4$ were carried out similarly.

(b) 3-(*p*-Anisylthio)propene, 3-((*p*-Fluorophenyl)thio)propene, and 3-((*p*-(Trifluoromethyl)phenyl)thio)propene. A mixture of $RhH(PPh_3)_4$ (610 mg, 0.53 mmol), 3-(*p*-anisylthio)propene (100 mg, 0.56 mmol), and toluene (15 mL) was stirred under vacuum at room temperature, similar to the reaction of 3-(phenylthio)propene. After measurement of the evolved propylene (96%/Rh) by GLC, the solvent was evaporated (to ca. 2 mL) under reduced pressure. To the residual red solution was added Et_2O (4 mL) to give orange microcrystals of $[Rh(\mu\text{-}SC_6H_4OCH_3)(PPh_3)_2]_2$ (3) which were washed twice with Et_2O and dried in vacuo (370 mg, 0.24 mmol, 91%). Recrystallization from a toluene–Et_2O (1:2) mixture gave orange prisms of 3.

Complexes 4 and 5 were obtained from reactions of 3-((*p*-fluorophenyl)thio)propene and 3-((*p*-(trifluoromethyl)phenyl)thio)propene, respectively, in a similar manner.

Reactions of CH_3I and C_6H_5I with 1. To a Schlenk tube containing 1 (101 mg, 0.070 mmol) and toluene (5 mL) was added CH_3I (4.6 g, 32 mmol) at room temperature. Stirring for 50 h at this temperature caused the formation of (methylthio)benzene (15 mg, 88%/Rh) (by GLC using diphenylmethane as an internal standard).

The reaction of C_6H_5I with 1 was carried out analogously at 100 °C (5 h) to give diphenyl sulfide (78%).

Similarly, the reaction of C_6H_5I with 2 at 100 °C (2 h) gave *p*-(phenylthio)toluene (83%/Rh).

Reaction of CO with 1, 2, and 3. Carbon monoxide was introduced to a Schlenk tube containing 390 mg of 1 and toluene (4 mL) at ambient pressure. Stirring at room temperature for 3 h resulted in the complete dissolution of 1 to give an orange solution. Evaporation of toluene (to ca. 1 mL) followed by addition of Et_2O (10 mL) gave orange-yellow crystals (180 mg, 69%), which were characterized as a mixture of **6a** and **6b** by elemental analysis, IR and NMR spectra, and molecular weight measurement.

Reaction of CO with 2 and 3 were performed analogously.

Reaction of 3-(Phenylthio)propene with $RhD(P(C_6D_5)_3)_4$. A reaction of 3-(phenylthio)propene (76 mg, 0.51 mmol) with $RhD(P(C_6D_5)_3)_4$ (210 mg, 0.17 mmol) was carried out in toluene under vacuum similar to the reaction of 3-(phenylthio)propene with $RhH(PPh_3)_4$. After the mixture was stirred for 24 h at room temperature, the deuterium content of the evolved propylene (93%/Rh) was measured by means of GC–MS using FI ion source. 3-(Phenylthio)propene remained in the reaction mixture was also measured by GC–MS (EI ion source) so as to show similar total ion current in each measurement and the content of deuterium was obtained by comparison of relative intensities of the peaks at m/e 150, 151, 152, and 153 with those of nondeuterated 3-(phenylthio)propene.

After removal of the solvent, aqueous H_2O_2 (35%, 3 mL) was added in order to release the PPh_3 ligand by oxidizing it to $O{=}PPh_3$, which was extracted with Et_2O, dried, and washed with a small amount of hot benzene to remove the contaminating allyl phenyl sulfone.[23] The ^1H content in $O{=}PPh_3$ thus obtained was measured by comparison of peak areas in ^1H and $^{31}P\{^1H\}$ NMR spectra using triethyl phosphite as an internal standard.

Reaction of Vinylic Aryl Sulfide with $RhH(PPh_3)_4$. To a Schlenk tube containing $RhH(PPh_3)_4$ (496 mg, 0.43 mmol) and toluene (15 mL) was added 1-(phenylthio)propene (65 mg, 0.43 mmol) at −195 °C. After evacuation of the flask, stirring was continued at room temperature. In 2 h $RhH(PPh_3)_4$ was dissolved completely to give a deep red solution. After 24 h, the propylene (0.10 mmol, 23%/Rh) evolved in the gas phase was measured by GLC. The benzene formed was analyzed by GC–MS, and its amount was measured by GLC using mesitylene as an internal standard.

Reaction of $RhH(PPh_3)_4$ with the other vinylic aryl sulfides were carried out analogously.

Registry No. 1, 92922-07-1; 2, 92922-08-2; 3, 92922-35-5; 4, 95251-29-9; 5, 95251-30-2; **6a**, 95251-31-3; **6b**, 95403-32-0; **7a**, 95251-32-4; **7b**, 95403-38-6; **8a**, 95251-33-5; **8b**, 95342-15-7; $RhH(PPh_3)_4$, 18284-36-1; $RhH(CO)(PPh_3)_3$, 17185-29-4; $CoH(N_2)(PPh_3)_3$, 32145-79-2; $RuHz(PPh_3)_4$, 19529-00-1; PhSH, 108-98-5; PhSSPh, 882-33-7; CH_3I, 74-88-4; C_6H_5I, 591-50-4; $PhCH_3$, 108-88-3; C_2H_4, 74-85-1; MeSPh, 100-68-5; Ph_2S, 139-66-2; C_6H_6, 71-43-2; propene, 115-07-1; 1-butene, 106-98-9; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; 3-methyl-1-butene, 563-45-1; 2-methyl-2-butene, 513-35-9; 2-methylpropene, 115-11-7; 3-phenyl-1-propene, 300-57-2; (*E*)-1–phenyl-1-propene, 873-66-5; *p*-(phenylthio)toluene, 3699-01-2; 3-(phenylthio)propene, 5296-64-0; 3-((4-methylphenyl)thio)propene, 1516-28-5; 3-((2-methylphenyl)thio)propene, 24309-31-7; 3-((4-methoxyphenyl)thio)propene, 37780-82-8; 3-((4-fluorophenyl)thio)propene, 2968-14-1; 3-((4-(trifluoromethyl)phenyl)thio)propene, 95274-95-6; (*E*)-1-(phenylthio)–2–butene, 36195-56-9; (*Z*)-1-(phenylthio)-2-butene, 36195-55-8; 3-(phenylthio)-1-butene, 701-75-7; 2-methyl-1-(phenylthio)-2-butene, 10276-04-7; 2-((phenylthio)methyl)propene, 702-00-1; (*E*)-1-phenyl-3-(phenylthio)propene, 5848-60-2; 1-(phenylthio)propene, 22103-05-5; 1–((4-(methylphenyl)thio)propene, 39815-00-4; (phenylthio)ethene, 1822-73-7.

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