Highly Regio- and Stereocontrolled Synthesis of Vinyl Sulfides via Transition-Metal-Catalyzed Hydrothiolation of Alkynes with Thiols

Akiya Ogawa,* Takuma Ikeda, Kouichi Kimura, and Toshikazu Hirao*

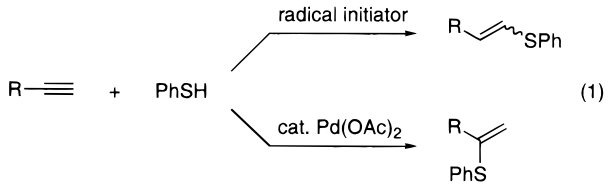
Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Received November 16, 1998

Abstract: Regio- and stereoselectivity in the hydrothiolation of alkynes with thiols in the presence of a variety of transition-metal catalysts is investigated in detail. Among the catalysts employed, $RhCl(PPh_3)_3$ exhibits excellent catalytic ability toward the anti-Markovnikov addition of thiols (ArSH) to alkynes (RC≡CH), which affords the corresponding vinylic sulfides (*trans*-RCH═CHSAr) regio- and stereoselectively. The reaction may proceed by the formation of hydrorhodium sulfide species (H−[Rh]−SAr) and probably via the subsequent hydrorhodation of alkynes to provide vinylrhodium intermediates (RCH═CH−[Rh]−SAr). In contrast, $PdCl_2(PhCN)_2$-catalyzed hydrothiolation of aromatic alkynes (ArC≡CH) takes place to give the corresponding Markovnikov adducts (R(ArS)C═CH_2) with excellent regioselectivity, probably via thiopalladation of alkynes by palladium sulfide species (ArS−[Pd]−Cl), which may be formed by ligand-exchange reaction between $PdCl_2(PhCN)_2$ and ArSH. Furthermore, in the case of alkynes bearing propargylic protons (R′CH_2C≡CH), a sequential addition/isomerization reaction occurs to provide the internal vinylic sulfides (R′CH═C(SAr)CH_3) regioselectively. From the same starting materials (alkyne and thiol), therefore, the regioselectivity of hydrothiolation can be attained simply by changing the catalysts, i.e., $RhCl(PPh_3)_3$ and $PdCl_2(PhCN)_2$.

Introduction

Although organic thiols have been widely employed as the sources of ligands for various transition metals,[1] the transition-metal-catalyzed reactions using them as substrates have been scarcely developed.[2] This is partly due to the widespread belief that organic sulfur compounds often bind strongly to the catalysts, thus poisoning them and making catalytic reactions ineffective. The addition of thiols to alkynes is one of the most straightforward methods of obtaining vinylic sulfides, which are important synthetic intermediates.[3] It is well-known that thiols add to alkynes under radical conditions to afford anti-Markovnikov-type vinylic sulfides with excellent regioselectivity, usually as a stereoisomeric mixture (eq 1).[4] In contrast to this,



we have recently revealed that the addition of thiols to terminal alkynes in the presence of a catalytic amount of palladium(II) acetate ($Pd(OAc)_2$) proceeds with a different regioselectivity to afford the corresponding Markovnikov adducts in high yields (eq 1).[5]

The mechanistic pathway given in Scheme 1 is proposed, on the basis of the following facts: (i) the stoichiometric reaction

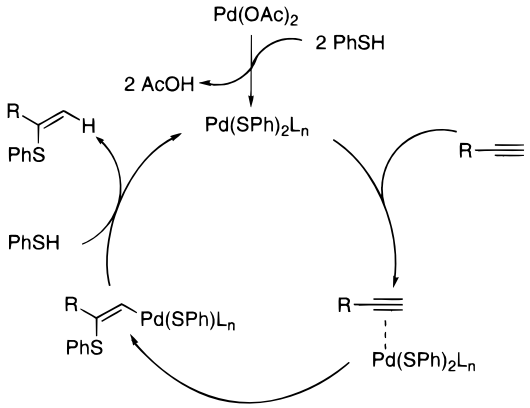
(1) (a) Linford, L.; Raubenheimer, H. G. In *Advances in Organometallic Chemistry;* Stone, F. G. A., West, R., Eds.; Academic Press: San Diego, CA, 1991; Vol. 32, p 1. (b) Stiefel, E. I.; Matsumoto, K., Eds. *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; ACS Symp. Ser. 653; American Chemical Society: Washington, DC, 1996. (c) Rakowski Dubois, M. *Chem. Rev.* **1989**, *89*, 1.

(2) (a) Holmquist, H. E.; Carnahan, J. E. *J. Org. Chem.* **1960**, *25*, 2240. (b) Talley, J. J.; Colley, A. M. *J. Organomet. Chem.* **1981**, *215*, C38. (c) McKervey, M. A.; Ratananukul, P. *Tetrahedron Lett.* **1982**, *23*, 2509. (d) Dzhemilev, U. M.; Kunakova, R. V.; Gaisin, R. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, *11*, 2655. (e) Shim, S. C.; Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 1935. (f) Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 2609. (g) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147. (h) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (i) Antebi, S.; Alper, H. *Can. J. Chem.* **1986**, *64*, 2010. (j) Iqbal, J.; Pandey, A.; Shukla, A.; Srivastava, R. R.; Tripathi, S. *Tetrahedron* **1990**, *46*, 6423. (k) Goux, C.; Lhoste, P.; Sinou, D. *Tetrahedron Lett.* **1992**, *33*, 8099. (l) Ogawa, A.; Sonoda, N. *J. Synth. Org. Chem. Jpn.* **1993**, *51*, 815. (m) Bäckvall, J.-E.; Ericsson, A. *J. Org. Chem.* **1994**, *59*, 5850. (n) Ogawa, A.; Takeba, M.; Kawakami, J.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1995**, *117*, 7564. (o) Ogawa, A.; Kawakami, J.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1996**, *61*, 4161. (p) Ogawa, A.; Kawakami, J.; Mihara, M.; Ikeda, T.; Sonoda, N. Hirao, T. *J. Am. Chem. Soc.* **1997**, *119*, 12380. (q) Xiao, W.-J.; Alper, H. *J. Org. Chem.* **1997**, *62*, 3422. (r) Xiao, W.-J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1998**, *63*, 2609. (s) Ogawa, A.; Kawabe, K.; Kawakami, J.; Mihara, M.; Hirao, T. *Organometallics* **1998**, *17*, 3111.

(3) For the synthetic utility of vinyl sulfides, see, for example: (a) Ager, D. J. *Chem. Soc. Rev.* **1982**, *11*, 493. (b) Takeda, T.; Furukawa, H.; Fujimori, M.; Suzuki, K.; Fujiwara, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1863. (c) Gröbel, B.-T.; Seebach, D. *Synthesis* **1977**, 357. (d) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075. (e) Magnus, P.; Quagliato, D. *J. Org. Chem.* **1985**, *50*, 1621. (f) De Lucchi, O.; Pasquato, L. *Tetrahedron* **1988**, *44*, 6755. (g) Pettit, G. R.; van Tamelen, E. E. *Org. React.* **1962**, *12*, 356. (h) Boar, R. B.; Hawkins, D. W.; McGhie, J. F.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 654. (i) Trost, B. M.; Ornstein, P. L. *Tetrahedron Lett.* **1981**, *22*, 3463. (j) Wenkert, E.; Ferreira, T. W. *J. Chem. Soc., Chem. Commun.* **1982**, 840. (k) Hojo, M.; Tanimoto, S. *J. Chem. Soc., Chem. Commun.* **1990**, 1284. (l) Hojo, M.; Harada, H.; Yoshizawa, J.; Hosomi, A. *J. Org. Chem.* **1993**, *58*, 6541.

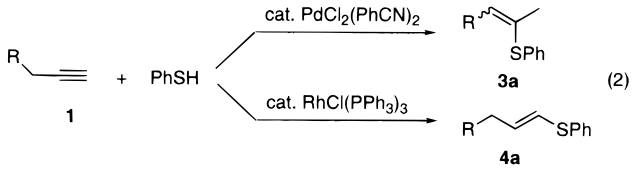
10.1021/ja983949i CCC: $18.00
Published on Web 05/18/1999

Scheme 1. Possible Pathway for $Pd(OAc)_2$-Catalyzed Hydrothiolation



of $Pd(OAc)_2$ with benzenethiol (2 equiv) provides palladium sulfide species ($[Pd(SPh)_2]_n$) and AcOH (2 equiv); (ii) a catalytic hydrothiolation of alkynes with PhSH can proceed using the palladium sulfide species as the catalyst. A possible catalytic pathway involves the ligand-exchange reaction between $Pd(OAc)_2$ and PhSH to generate palladium sulfide species ($[Pd(SPh)_2]_n$) with concomitant formation of acetic acid, followed by regioselective thiopalladation of alkynes to give the corresponding vinylic palladium intermediate. The subsequent protonation of the vinylic palladium species with PhSH provides the Markovnikov-type vinylic sulfide with regeneration of the palladium sulfide catalyst. Thus, the radical reaction and the $Pd(OAc)_2$-catalyzed reaction are complementary to each other for the regioselective synthesis of vinylic sulfides from the same starting materials, *i.e.*, alkynes and thiols.

In this paper, we wish to report that, when $PdCl_2(PhCN)_2$ is used as a catalyst, a novel Markovnikov addition and double-bond isomerization reaction of benzenethiol with terminal alkynes is found to take place sequentially, which provides a useful tool for preparing internal vinylic sulfides (**3**) (eq 2). More



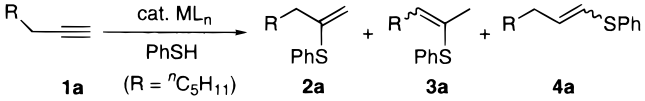
(2)

interestingly, switching the catalyst simply from $Pd(OAc)_2$ to $RhCl(PPh_3)_3$ leads to a sharp reversal of regioselectivity in the addition of PhSH to alkynes, providing anti-Markovnikov-type vinylic sulfides (**4**) with the trans configuration (eq 2).

Results and Discussion

Influence of Catalysts on the Hydrothiolation of 1-Octyne with Benzenethiol. The reaction of benzenethiol with 1-octyne (**1a**) was examined in the presence of several transition-metal catalysts, and the results are summarized in Table 1.

Table 1. Transition-Metal-Catalyzed Addition of PhSH to 1-Octyne[a]

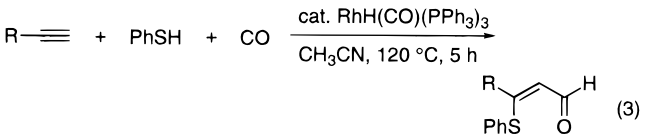


1a **2a** **3a** **4a**

		yield, %[b]		
entry no.	catalyst	**2a**	**3a** [*E*/*Z*]	**4a** [*E*/*Z*]
1[c]	$Pd(OAc)_2$	85	trace	trace
2	$PdCl_2(PhCN)_2$	1	66 [56/44]	0
3	$PdCl_2(MeCN)_2$	2	58 [64/36]	23 [51/49]
4	$Pd(PPh_3)_4$	17	2	16 [91/9]
5	$Pt(PPh_3)_2(CH_2{=}CH_2)$	19	38 [63/37]	17 [50/50]
6[d]	$Pt(PPh_3)_2(CH_2{=}CH_2)$	41	10 [76/24]	5 [40/60]
7	$RhH(CO)(PPh_3)_3$	49	0	16 [76/24]
8[d]	$RhH(CO)(PPh_3)_3$	19	26 [61/39]	14 [89/11]
9[e]	$RhH(CO)(PPh_3)_3$	2	58 [67/33]	7 [43/57]
10	$RhCl(PPh_3)_3$	29	0	50 [100/0]
11[f]		0	0	65 [48/52]

[a] Reaction conditions: 1-octyne (1 mmol), PhSH (1 mmol), catalyst (5 mol %), benzene (0.5 mL), 80 °C, 20 h. [b] Determined by ^1H NMR. [c] Catalyst (2 mol %), THF (0.5 mL), 40 °C. [d] Catalyst (3 mol %). [e] Catalyst (0.5 mol %). [f] In the absence of catalysts.

As mentioned already, $Pd(OAc)_2$ effects the Markovnikov addition of PhSH to **1a** (entry 1). On the other hand, some other divalent palladium complexes, especially $PdCl_2(PhCN)_2$, exhibited excellent catalytic activity for the sequential Markovnikov addition and double-bond isomerization to afford the corresponding internal vinylic sulfides (**3a**) selectively (entries 2 and 3). In contrast, palladium(0) and platinum(0) catalysts did not indicate the product selectivity at all (entries 4−6). In the case of the former catalyst, 10−15% of *vic*-bis(phenylthio)-1-octene was also obtained. In the case of the latter catalyst, the product selectivity was dependent on amounts of the catalyst employed: the double-bond isomerization of **2a** to **3a** was depressed by decreasing the catalyst (entry 6). As reported previously,[2n] $RhH(CO)(PPh_3)_3$ is an excellent catalyst for the regioselective thioformylation of alkynes with benzenethiol in the presence of carbon monoxide (eq 3). In contrast to our



(3)

expectation that the catalyst may exhibit the excellent regioselectivity in the hydrothiolation, however, the addition of PhSH to **1a** in the presence of this rhodium catalyst provided both Markovnikov and anti-Markovnikov adducts (**2a**, **3a**, and **4a**, respectively), where the formation ratio of **2a** vs **3a** depended on the amounts of the catalyst employed (entries 7−9).

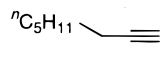
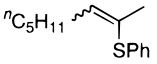
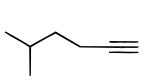
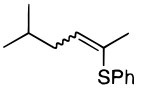
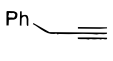
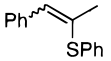
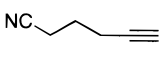
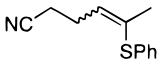
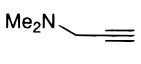
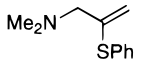
Similarly, Wilkinson catalyst ($RhCl(PPh_3)_3$) also gave rise to both Markovnikov and anti-Markovnikov adducts (**2a** and **4a**), but the fact that the stereochemistry of **4a** was only *E* is noteworthy (entry 10). In the absence of catalyst, the reaction of PhSH with 1-octyne in refluxing benzene afforded the corresponding anti-Markovnikov adduct as a stereoisomeric mixture (entry 11). In contrast to this, the use of $PdCl_2(PhCN)_2$ or $Pd(OAc)_2$ led to a sharp reversal of regioselectivity of the hydrothiolation, whereas the $RhCl(PPh_3)_3$-catalyzed hydrothiolation proceeded with excellent stereoselectivity.

$PdCl_2(PhCN)_2$-Catalyzed Sequential Addition/Isomerization Reaction of Benzenethiol with Terminal Alkynes. Table

(4) (a) Peach, M. E. In *The Chemistry of the Thiol Group;* Patai, S., Ed.; Wiley: London, 1974; Vol. 2. (b) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J.-L.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1987**, 1647. (c) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1035. (d) Griesbaum, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 273 and references therein.

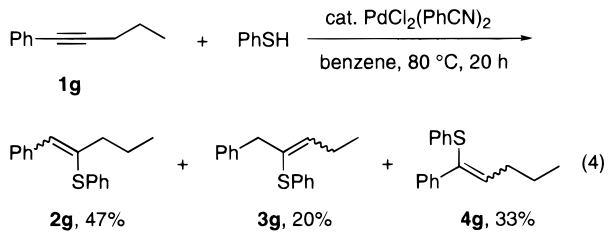
(5) (a) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902. Also, see: (b) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Sonoda, N. *Tetrahedron Lett.* **1992**, *33*, 5525. (c) Ogawa, A.; Kudo, A.; Hirao. T. *Tetrahedron Lett.* **1998**, *39*, 5213, and refs 2l,m,o.

Table 2. $PdCl_2(PhCN)_2$-Catalyzed Sequential Addition/Isomerization Reactions[a]

entry	acetylene	product	yield, % [*E*/*Z*][b]
1	 **1a**	 **3a**	66 [56/44]
2	 **1b**	 **3b**	77 [58/42]
3	 **1c**	 **3c**	70 [55/45]
4	 **1d**	 **3d**	63 [40/60]
5	 **1e**	 **2e**	69
6	 **1f**	 **2f**	68

[a] Reaction conditions: alkyne (1 mmol), PhSH (1 mmol), $PdCl_2(PhCN)_2$ (5 mol %), benzene (0.5 mL), 80 °C, 20 h. [b] *E*/*Z* ratio was determined by ^1H NMR.

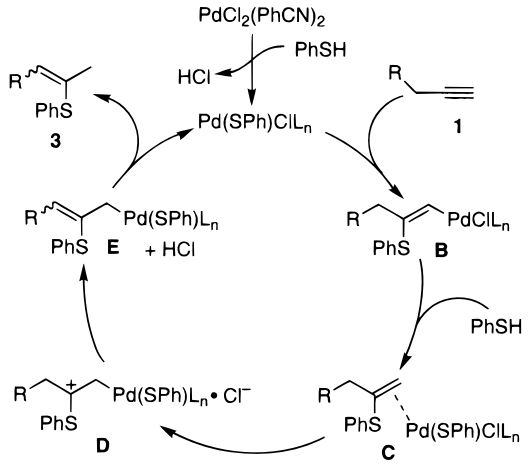
2 represents the sequential addition/isomerization reactions of terminal alkynes in the presence of $PdCl_2(PhCN)_2$. 5-Methyl-1-hexyne (**1b**) and benzylacetylene (**1c**) were selectively converted to 2-(phenylthio)-5-methyl-2-hexene (**3b**) and 2-(phenylthio)-2-methylstyrene (**3c**), respectively, in good yields (entries 2 and 3). Similar conditions can be employed with an alkyne (**1d**) bearing a cyano group, giving the corresponding internal vinylic sulfide (**3d**) regioselectively (entry 4). However, hydrothiolation of propargyldimethylamine (**1e**) provided only Markovnikov adduct (**2e**) regioselectively in 69% yield; this indicates that the presence of a basic amino group inhibits the double-bond isomerization entirely (entry 5). On the other hand, alkynes bearing no propargylic protons, such as phenylacetylene (**1f**), underwent regioselective hydrothiolation to provide Markovnikov adduct (**2f**) in good yield (entry 6). In the case of an inner alkyne (**1g**), hydrothiolation proceeded to give three regioisomeric adducts (**2g**, **3g**, and **4g**), as shown in eq 4.



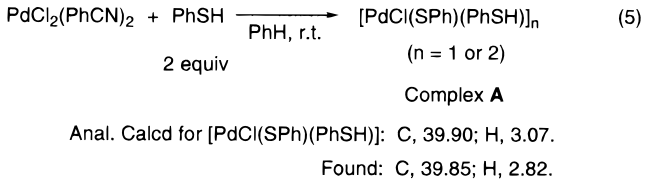
(4)

To get some information about this sequential addition/isomerization reaction, the stoichiometric reaction of $PdCl_2(PhCN)_2$ with 2 equiv of PhSH in benzene at room temperature was conducted. The reaction provided a reddish brown solid,

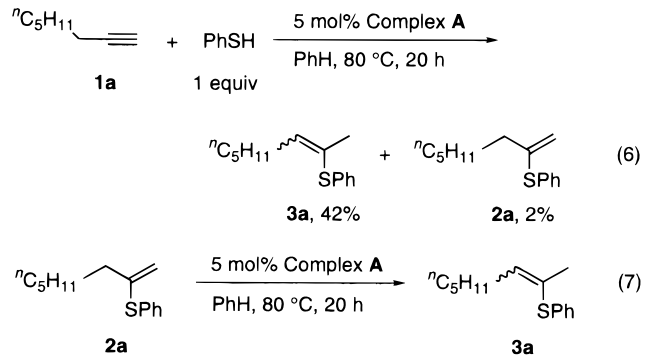
Scheme 2. Possible Pathway for $PdCl_2(PhCN)_2$-Catalyzed Hydrothiolation



the elemental analysis of which suggests the formation of the palladium sulfide complex **A**, as depicted in eq 5 (see also the Experimental Section). The reaction of benzenethiol with



(5)



1-octyne (**1a**) in the presence of the complex **A** as a catalyst afforded the corresponding addition/isomerization product **3a** in 42% yield (eq 6). In addition, treatment of the Markovnikov adduct **2a** in the presence of a catalytic amount of complex **A** resulted in the double-bond isomerization to give **3a** in almost quantitative yield (eq 7).[6] These observations suggest that the complex **A** is an excellent catalyst for the double-bond isomerization reaction and also exhibits a moderate catalytic activity toward the Markovnikov addition reaction of thiols to alkynes.

Scheme 2 illustrates a possible reaction pathway for the $PdCl_2(PhCN)_2$-catalyzed hydrothiolation of alkynes, which includes the following: (i) the ligand-exchange reaction of $PdCl_2(PhCN)_2$ with PhSH forms $Pd(SPh)ClL_n$, which adds to alkyne **1**, providing vinylic palladium intermediate **B**; (ii) protonation of **B** with PhSH leads to the Markovnikov type adduct **C**; (iii) double-bond isomerization of **C** to **3** takes place via cationic intermediate **D**[6] and allylpalladium intermediate **E**.

$RhCl(PPh_3)_3$-Catalyzed anti-Markovnikov Addition of Thiols to Alkynes. As mentioned in Table 1, the $RhCl(PPh_3)_3$-

(6) (a) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1981**, *20*, 4036. (b) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1984**, *23*, 3257.

Table 3. $RhCl(PPh_3)_3$-Catalyzed Regio- and Stereoselective Addition of PhSH to 1-Octyne[a]

				yield, %[b]		
entry no.	solvent	temp, °C	additive (amt, mol %)	**2a**	**3a**	**4a** [*E*/*Z*]
1	PhH	80		29	0	50 [100/0]
2[c]	PhH	80		15	11	65 [99/1]
3	PhH	40		19	0	54 [100/0]
4	$PhCH_3$	110		17	4	20 [98/2]
5	THF	67		9	15	60 [100/0]
6	$PhCF_3$	40		5	7	49 [100/0]
7	CH_2Cl_2	40		22	0	76 [100/0]
8	$(CH_2Cl)_2$	40		11	4	58 [100/0]
9	DMF	100		0	16	39 [100/0]
10	CH_3CN	40		2	23	40 [96/4]
11	EtOH	78		0	9	58 [100/0]
12[d]	EtOH	25		0	3	69 [100/0]
13[e]	EtOH	25		0	4	80 [100/0]
14	EtOH	25	PPh_3 (30)	36	0	53 [100/0]
15	EtOH	25	PPh_3 (10)	34	0	60 [100/0]
16	EtOH	25	P(tol-*o*)$_3$ (30)	21	0	63 [100/0]
17	EtOH	25	PBu^n_3 (30)	19	0	31 [100/0]
18[f]	EtOH	25		26	0	69 [100/0]
19	EtOH	25	galvinoxyl (3)	0	0	73 [100/0]
20[g]	EtOH	25			no reacn	

[a] Reaction conditions: 1-octyne (1 mmol), PhSH (1.1 mmol), $RhCl(PPh_3)_3$ (5 mol %), solvent (0.5 mL), 20 h. [b] Determined by ^1H NMR. [c] Catalyst (10 mol %). [d] $(PhS)_2$ was formed as a byproduct. [e] PhSH was added dropwise. [f] *o*-CH_3-C_6H_4SH was used in place of PhSH. [g] In the absence of $RhCl(PPh_3)_3$ catalyst.

catalyzed hydrothiolation of 1-octyne (**1a**) with PhSH provided (*E*)-1-(phenylthio)-1-octene (**4a**) along with its regioisomer (**2a**) (see Table 1, entry 10). Thus, we next investigated in detail the $RhCl(PPh_3)_3$-catalyzed hydrothiolation under various reaction conditions (Table 3). The influence of the solvents on the $RhCl(PPh_3)_3$-catalyzed hydrothiolation was examined (entries 1−11), and, among the solvents employed (PhH, PhMe, THF, BTF,[7] CH_2Cl_2, $(CH_2Cl)_2$, DMF, MeCN, EtOH), the use of EtOH realized the highest product selectivity of (*E*)-**4a** (entry 11). When the hydrothiolation was conducted in EtOH at a lower temperature, a better selectivity of (*E*)-**4a** was observed (entry 12). In this reaction, however, $(PhS)_2$ (ca. 20%) was formed as a byproduct. The dropwise addition of PhSH is expected to depress the formation of $(PhS)_2$. Thus, the best result was obtained when a slight excess of PhSH was added dropwise at 25 °C over 1 h to the solution of 1-octyne and $RhCl(PPh_3)_3$ (5 mol %) in EtOH (entry 13). Moreover, the influence of the bulkiness of ligands and thiols on the selectivity of the hydrothiolation was investigated. Although the addition of phosphines to the catalytic system decreased the selectivity of the hydrothiolation (entries 14 and 15), the use of more bulky phosphine did not improve the regioselectivity (entries 16 and 17). Similarly, the use of *o*-methylbenzenethiol in place of PhSH also decreased the selectivity (entry 18). To rule out the possibility that a radical mechanism contributes to this anti-Markovnikov addition process, the rhodium-catalyzed reaction of PhSH to alkynes was examined in the presence of a radical inhibitor such as galvinoxyl (entry 19). The reaction proceeded smoothly to provide the anti-Markovnikov adduct regio- and stereoselectively. In the absence of the rhodium catalyst, the reaction of PhSH with alkynes in EtOH resulted in only recovery of the starting materials (entry 20). These observations clearly indicate that the present anti-Markovnikov addition process proceeds as a catalytic reaction of $RhCl(PPh_3)_3$.

(7) Ogawa, A.; Curran, D. P. *J. Org. Chem.* **1997**, *62*, 450.

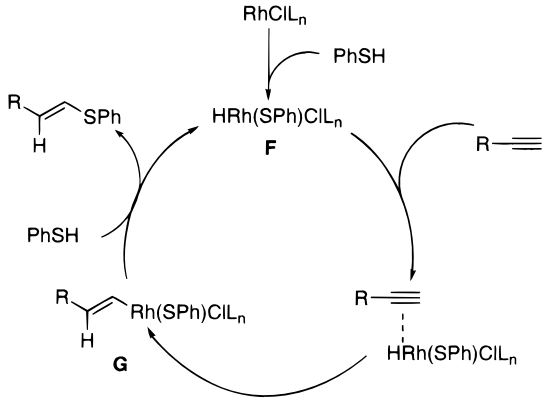
Table 4. $RhCl(PPh_3)_3$-Catalyzed Regio- and Stereoselective Addition of PhSH to Acetylenes[a]

entry	acetylene	temp, °C	product, **4**	yield, %[b]
1	**1f** (X = H)	40	**4f** (X = H)	97
2	**1h** (X = Me)	20	**4h** (X = Me)	94
3	**1i** (X = F)	20	**4i** (X = F)	75
4	**1j**	25	**4j**	80[c]
5[d]	**1j**	30	**4j'** (X = MeO)	72[c]
6[e]	**1j**	40	**4j''** (X = Cl)	86[c]
7	**1b**	25	**4b**	66[c]
8	**1k**	25	**4k**	62
9	**1l**	40	**4l**	67
10	**1m**	20	**4m**	73
11	**1n**	20	**4n**	80[c]
12	**1o**	20	**4o**	97[c]

[a] Reaction conditions: alkyne (1 mmol), PhSH (1.1 mmol), $RhCl(PPh_3)_3$ (1−3 mol %), EtOH (1 mL), 20 h. [b] Isolated yield based on the thiol used. [c] Thiol was added dropwise over 1 h. [d] *p*-MeO-C_6H_4SH was used. [e] *p*-Cl-C_6H_4SH was used.

Table 4 represents the results of the $RhCl(PPh_3)_3$-catalyzed addition of ArSH to a series of alkynes. The procedure can be applied to both aromatic and aliphatic alkynes. Similarly, arenethiols bearing *p*-methoxy and *p*-chloro groups add to alkynes regio- and stereoselectively (entries 5 and 6). In contrast, the hydrothiolation with alkanethiols such as cyclohexanethiol did not proceed at all under the same conditions, and most of the starting materials were recovered unchanged. Inner alkynes such as **1n** and **1o** underwent stereoselective hydrothiolation, and in particular, excellent regioselectivity was also observed in the hydrothiolation of **1o** (entries 11 and 12). Functionalities such as fluoro, chloro, hydroxy, methoxy, and olefinic groups tolerate the reaction conditions (entries 3, 5, 6, and 8−10). In all cases listed in Table 4, the addition proceeded with excellent regio- and stereoselectivity to provide only the *E* isomer of the anti-Markovnikov adduct **4**.

Scheme 3. Possible Pathway for $RhCl(PPh_3)_3$-Catalyzed Hydrothiolation



To explore the reaction pathway for this $RhCl(PPh_3)_3$-catalyzed hydrothiolation, the stoichiometric reaction of $RhCl(PPh_3)_3$ with benzenethiol was examined. The equimolar reaction of $RhCl(PPh_3)_3$ with PhSH at 20 °C in dichloromethane under an argon atmosphere afforded a yellow solid, which could be identified unambiguously as *trans*-$HRhCl(SPh)(PPh_3)_2$ (**F**), reported in the literature[8] (eq 8). The catalytic reaction of 1-dodecyne (**1j**) with benzenethiol in the presence of 3 mol % of complex **F** afforded the anti-Markovnikov adduct **4j** in good yield (eq 9).

$$RhCl(PPh_3)_3 + PhSH \xrightarrow[r.t.,\ 1\ h]{CH_2Cl_2} HRhCl(SPh)(PPh_3)_2 \quad (8)$$

Complex **F**

^{1}H NMR ($CDCl_3$) δ -16.4 ppm (Rh-H)

$$^nC_{10}H_{21}{-}\equiv + PhSH \xrightarrow[EtOH,\ 30\ °C,\ 20\ h]{3\ mol\%\ Complex\ F} {}^nC_{10}H_{21}\!\!\diagup\!\!=\!\!\diagdown SPh \quad (9)$$

1j 1.1 equiv **4j**, 55%

To gain further insight into the mechanistic pathway, the $RhCl(PPh_3)_3$-catalyzed hydrothiolation of 1-dodecyne (**1j**) with PhSH was monitored by ^{1}H NMR spectra. The reaction of complex **F** with an equimolar amount of **1j** at room temperature led to the disappearance of both Rh−*H* (δ −16.4) and acetylenic H, and instead, a new doublet peak appeared at δ 5.1 (probably as the vinylic proton). The new peak did not disappear after standing for 20 h at room temperature, but the addition of PhSH (1 equiv) to the solution led to the formation of vinylic sulfide (**4j**) after standing for 6 h. Thus, a possible catalytic cycle for this hydrothiolation of alkynes is shown in Scheme 3. Formation of H−[Rh]−SPh (**F**) occurred via the oxidative addition of PhSH to $RhClL_n$, followed by the stereoselective insertion of alkynes into the Rh−H bond to form the *trans*-vinylrhodium intermediate **G**. The subsequent reductive elimination of the anti-Markovnikov adduct, in the presence of excess PhSH, regenerates the catalyst **F**.

In conclusion, we have developed a highly selective anti-Markovnikov addition of benzenethiol to alkynes catalyzed by $RhCl(PPh_3)_3$, which is complementary to the previously reported $Pd(OAc)_2$-catalyzed Markovnikov addition of benzenethiol to acetylenes. Also, a useful sequential addition/isomerization reaction of benzenethiol with terminal alkynes is found to take place by employing $PdCl_2(PhCN)_2$ as a catalyst. From the same starting materials (alkyne and thiol), therefore, isomeric vinylic sulfides can be synthesized with excellent selectivity simply by switching the catalysts, i.e., $PdCl_2(PhCN)_2$ and $RhCl(PPh_3)_3$. This paper again demonstrates the utility of transition-metal catalysts in the synthetic reactions of sulfur compounds.

(8) Singer, H.; Wilkinson. G. *J. Chem. Soc. A* **1968**, 2516.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on Varian MERCURY 300 (300 MHz), JEOL JNM-AL400 (400 MHz), and JEOL JNM-GSX-400 (400 MHz) spectrometers using $CDCl_3$ as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra were taken on Varian MERCURY 300 (75 MHz) and JEOL JNM-AL400 (100 MHz) spectrometers using $CDCl_3$ as the solvent. Chemical shifts in ^{13}C NMR spectra were measured relative to $CDCl_3$ and converted to δ_{Me_4Si} values by using δ_{CDCl_3} 76.9 ppm. IR spectra were determined on a Perkin-Elmer Model 1600 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Mass spectra were obtained on a JEOL JMS-DX303 in the analytical section of our department. Elemental analyses were also performed there. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the complex **A** (obtained by the reaction of $PdCl_2(PhCN)_2$ with PhSH (2 equiv)) were determined using gel permeation chromatography (GPC). The GPC equipment (HLC-8020 system, Tosoh, Tokyo, Japan) consisted of an RI detector and Tosoh TSKgel α3000 and α5000. Calibration was carried out using narrow weight distribution PEG standards (Tosoh), ranging from ca. 2×10^2 to 9.9×10^5 g mol^{-1}. The eluent used was *N*,*N*-dimethylformamide (DMF; HPLC grade), at a flow rate of 0.5 mL min^{-1}.

All materials were obtained from commercial suppliers and purified by distillation or recrystallization.

General Procedure for the $PdCl_2(PhCN)_2$-Catalyzed Hydrothiolation of Alkynes with Thiols. In a 20 mL two-necked glass flask equipped with a condenser and a magnetic stirring bar under an argon atmosphere were placed $PdCl_2(PhCN)_2$ (5 mol %, 0.0192 g), benzene (0.5 mL), alkyne (1.0 mmol: **1a**, 0.110 g, 0.148 mL; **1b**, 0.0962 g, 0.132 mL; **1c**, 0.116 g, 0.124 mL; **1d**, 0.0931 g, 0.105 mL; **1e**, 0.0831 g, 0.105 mL; **1f**, 0.102 g, 0.110 mL; **1g**, 0.144 g, 0.155 mL), and benzenethiol (1.0 mmol, 0.110 g, 0.103 mL). The reaction was conducted with magnetic stirring for 20 h at 80 °C. After the reaction was complete, the resulting mixture was filtered through Celite and concentrated in vacuo. Purification was performed by a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC, using $CHCl_3$ as an eluent) or by preparative TLC (silica gel, hexane as an eluent).

2-(Phenylthio)-2-octene (3a): yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): (*E* isomer) δ 0.89 (t, J = 6.6 Hz, 3 H), 1.27−1.53 (m, 6 H), 1.90 (s, 3 H), 2.31 (q, J = 6.8 Hz, 2 H), 5.83 (t, J = 6.9 Hz, 1 H), 7.16−7.35 (m, 5 H); (*Z* isomer) δ 0.90 (t, J = 6.9 Hz, 3 H), 1.27−1.53 (m, 6 H), 1.87 (s, 3 H), 2.12 (q, J = 7.2 Hz, 2 H), 5.90 (t, J = 7.2 Hz, 1 H), 7.16−7.35 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E* isomer) δ 14.2, 22.6, 24.5, 29.2, 30.0, 31.6, 126.0, 128.3, 128.7, 129.9, 135.0, 136.0; (*Z* isomer) δ 14.2, 18.2, 22.6, 29.0, 29.4, 31.6, 126.1, 128.0, 128.7, 129.8, 135.5, 136.75. IR (NaCl): 3058, 2922, 2854, 1584, 1475, 1439, 741, 692 cm^{-1}. MS (EI): *m*/*z* 220 (M^+, 82.0). Anal. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15; S, 14.55. Found: C, 76.05; H, 9.09; S, 14.33.

2-(Phenylthio)-5-methyl-2-hexene (3b): yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): (*E* isomer) δ 0.93 (t, J = 6.6 Hz, 6 H), 1.70 (septet, J = 6.9 Hz, 1 H), 1.92 (q like, J = 1.5 Hz, 3 H), 2.23 (tq, J = 1.2, 7.2 Hz, 2 H), 5.84 (tq, J = 1.5, 6.9 Hz, 1 H), 7.16−7.33 (m, 5 H); (*Z* isomer) δ 0.93 (t, J = 6.6 Hz, 6 H), 1.70 (septet, J = 6.9 Hz, 1 H), 1.87 (quint like, J = 0.6 Hz, 3 H), 2.02 (t, J = 7.1 Hz, 2 H), 5.90 (tq, J = 1.5, 7.2 Hz, 1 H), 7.16−7.33 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E* isomer) δ 22.5, 24.6, 28.8, 39.1, 126.0, 128.7, 129.1, 130.0, 134.7, 135.0; (*Z* isomer) δ 18.3, 22.5, 28.7, 38.5, 126.2, 128.8, 129.9, 135.3, 135.4. IR (NaCl) 3070, 2954, 1583, 1476, 1438, 1382, 1067, 1025, 741, 692 cm^{-1}. MS (EI): *m*/*z* 206 (M^+, 72.4). Anal. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.53. Found: C, 75.55; H, 8.80; S, 15.36.

2-(Phenylthio)-2-methylstyrene (3c): yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): (*E* isomer) δ 2.13 (s, 3 H), 6.68 (s, 1 H), 7.19−7.56 (m, 10 H); (*Z* isomer) δ 2.03 (s, 3 H), 6.71 (s, 1 H), 7.19−7.56 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E* isomer) δ 19.7, 126.7, 127.3, 128.2, 128.6, 129.0, 130.7, 132.0, 133.7, 133.8, 137.0; (*Z* isomer) δ 25.8, 126.9, 127.1, 127.9, 128.8, 129.0, 130.8, 133.7, 136.7. IR (NaCl): 3056, 2914, 1582, 1475, 1439, 1099, 1025, 746, 693 cm^{-1}. MS (EI): *m*/*z* 226 (M^+, 100.0). Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.17. Found: C, 79.32; H, 6.13; S, 14.11.

2-(Phenylthio)-5-cyano-2-pentene (3d): yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): (*E* isomer) δ 1.92 (s, 3 H), 2.41 (t, J = 6.4 Hz, 2 H), 2.47 (q, J = 6.8 Hz, 2 H), 5.63 (t, J = 7.6 Hz, 1 H), 7.24−7.38 (m, 5 H); (*Z* isomer) δ 1.92 (s, 3 H), 2.44 (t, J = 7.2 Hz, 2 H), 2.68 (q, J = 6.8 Hz, 2 H), 5.80 (t, J = 6.8 Hz, 1 H), 7.24−7.43 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): (*E* isomer) δ 17.4, 18.1, 25.2, 118.9, 126.9, 127.2, 128.9, 131.6, 133.3, 134.2; (*Z* isomer) δ 17.4, 24.4, 25.7, 119.1, 126.8, 128.9, 129.1, 130.9, 133.2, 133.7. IR (NaCl): 3060, 2920, 2246, 1582, 1476, 1437, 1022, 747, 695 cm^{-1}. MS (EI): *m*/*z* 203 (M^+, 100.0). Anal. Calcd for $C_{12}H_{13}NS$: C, 70.90; H, 6.45; N, 6.89; S, 15.77. Found: C, 70.62; H, 6.36; N, 6.93; S, 15.59.

Stoichiometric Reaction of $PdCl_2(PhCN)_2$ with PhSH. In a 20 mL two-necked glass flask with a magnetic stirring bar under an argon atmosphere were placed $PdCl_2(PhCN)_2$ (0.1 mmol, 0.0384 g) and benzene (1 mL). Benzenethiol (0.2 mmol, 0.0220 g, 0.0205 mL) was added to the solution at room temperature, and the resulting mixture was stirred for 1 h. The resulting reddish brown precipitates were separated by filtration. After removal of the solvent, the ^{1}H NMR spectrum of the filtrate was measured, which indicated the formation of 2 equiv of PhCN. The reddish brown precipitates were rinsed with benzene several times and then dried under reduced pressure to yield the complex **A** almost quantitatively. Complex **A** (reddish brown solid): mp >300 °C. IR (KBr): 3049, 1573, 1472, 1435, 1297, 1064, 1021, 998, 734, 682 cm^{-1}. Anal. Calcd for [PdCl(SPh)(PhSH)]: C, 39.90; H, 3.07. Found: C, 39.85; H, 2.82. Complex **A** was insoluble in most organic solvents such as benzene, toluene, Et_2O, THF, CH_2Cl_2, $CHCl_3$, MeCN, acetone, DMSO, MeOH, EtOH, etc. Although **A** was slightly soluble in DMF (ca. 3 mM), the concentration was too dilute to measure its NMR spectra using d_6-DMF as a solvent. Thus, the ^{1}H and ^{13}C NMR spectra of the solid state form of **A** were measured (see the Supporting Information). Mass spectral analysis of **A** was unsuccessful because the appropriate matrix could not be found, due to the insolubility of **A** in most organic solvents. By using a dilute solution of **A** in DMF, however, its molecular weight could be assumed by using GPC (see General Methods). The number-average molecular weight (M_n) was 409 (M_w/M_n = 1.21), which indicates the possibility that **A** may be monomeric or dimeric but does not have a polymeric (or oligomeric) structure.

General Procedure for the $RhCl(PPh_3)_3$-Catalyzed Hydrothiolation of Alkynes with Thiols. In a 20 mL two-necked glass flask with a magnetic stirring bar under an argon atmosphere were placed $RhCl(PPh_3)_3$ (3 mol %, 0.0278 g), EtOH (1 mL), and alkyne (1.0 mmol: **1a**, 0.110 g, 0.148 mL; **1b**, 0.0962 g, 0.132 mL; **1f**, 0.102 g, 0.110 mL; **1h**, 0.116 g, 0.123 mL; **1i**, 0.120 g, 0.115 mL; **1j**, 0.163 g, 0.214 mL; **1k**, 0.0841 g, 0.0931 mL; **1l**, 0.103 g, 0.106 mL; **1m**, 0.106 g, 0.118 mL; **1n**, 0.110 g, 0.148 mL; **1o**, 0.116 g, 0.125 mL), and then thiol (1.1 mmol, neat: PhSH, 0.121 g, 0.113 mL; *p*-$MeOC_6H_4SH$, 0.154 g, 0.135 mL; *p*-ClC_6H_4SH, 0.159 g; *o*-MeC_6H_4SH, 0.137 g, 0.130 mL) was added dropwise to the solution over 1 h at room temperature (25 °C). The reaction was continued with magnetic stirring for 20 h at room temperature. After the reaction was complete, the solvent was removed in vacuo. Purification was performed by a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC, using $CHCl_3$ as an eluent) or by preparative TLC (silica gel, hexane as an eluent).

(*E*)-1-(Phenylthio)-1-octene (4a): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, J = 6.9 Hz, 3 H), 1.20−1.37 (m, 6 H), 1.42 (br quint, J = 7.5 Hz, 2 H), 2.15 (dt, J = 6.6, 7.5 Hz, 2 H), 6.00 (dt, J = 6.6, 15.0 Hz, 1 H), 6.13 (dt, J = 1.2, 14.7 Hz, 1 H), 7.14−7.35 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 22.7, 28.9, 29.1, 31.7, 33.2, 120.5, 125.9, 126.0, 128.3, 128.8, 137.8. IR (NaCl): 3059, 2927, 2854, 1583, 1478, 1439, 1090, 1025, 949, 738, 690 cm^{-1}. MS (EI): *m*/*z* 220 (M^+, 91.0). Anal. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15; S, 14.55. Found: C, 76.29; H, 9.10; S, 14.44.

(*E*)-2-(Phenylthio)styrene (4f): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.73 (d, J = 15.3 Hz, 1 H), 6.86 (d, J = 15.3 Hz, 1 H), 7.17−7.44 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 123.3, 125.9, 126.8, 127.5, 128.6, 129.0, 129.7, 131.7, 135.1, 136.4;. IR (NaCl): 3059, 3030, 1583, 1479, 1442, 1086, 946, 742, 693 cm^{-1}. MS (EI): *m*/*z* 212 (M^+, 100.0). Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70; S, 15.10. Found: C, 79.21; H, 5.74; S, 15.25.

(*E*)-2-(Phenylthio)-*p*-methylstyrene (4h): white solid; mp 46.2−47.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3 H), 6.76 (d, J = 15.3 Hz, 1 H), 6.86 (d, J = 15.3 Hz, 1 H), 7.16 (d, J = 8.4 Hz, 2 H), 7.27−7.45 (m, 7 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 121.8, 125.9, 126.7, 129.0, 129.3, 129.4, 132.3, 133.7, 135.5, 137.5. IR (KBr): 3018, 1580, 1509, 1477, 1436, 958, 790, 734, 689 cm^{-1}. MS (EI): *m*/*z* 226 (M^+, 100.0). Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.16. Found: C, 79.41; H, 5.93; S, 14.11.

(*E*)-2-(Phenylthio)-*p*-fluorostyrene (4i): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.73 (d, J = 15.3 Hz, 1 H), 6.84 (d, J = 15.3 Hz, 1 H), 7.05 (t like, J = 8.7 Hz, 2 H), 7.27−7.47 (m, 7 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.5 (d, J_{C-F} = 21.6 Hz), 123.0, 126.9, 127.4 (d, J_{C-F} = 8.0 Hz), 129.1, 129.7, 130.5, 132.6, 134.9, 162.0 (d, J_{C-F} = 255.0 Hz). IR (NaCl): 3062, 1601, 1580, 1507, 1478, 1229, 1158, 949, 840, 741, 691 cm^{-1}. MS (EI): *m*/*z* 230 (M^+, 100.0). Anal. Calcd for $C_{14}H_{11}FS$: C, 73.01; H, 4.81. Found: C, 72.79; H, 4.86.

(*E*)-1-(Phenylthio)-1-dodecene (4j): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.20−1.39 (m, 14 H), 1.40 (br quint, J = 6.9 Hz, 2 H), 2.15 (t, J = 6.6 Hz, 2 H), 6.00 (td, J = 6.6, 15.0 Hz, 1 H), 6.13 (td, J = 0.9, 15.3 Hz, 1 H), 7.16−7.33 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.8, 29.1, 29.2, 29.4, 29.5, 29.7, 32.0, 33.2, 120.5, 125.9, 128.2, 128.8, 136.6, 137.8. IR (NaCl): 3082, 2925, 2853, 1584, 1478, 1439, 1090, 1025, 949, 738, 690 cm^{-1}. MS (EI): *m*/*z* = 276 (M^+, 100.0). Anal. Calcd for $C_{18}H_{28}S$: C, 78.20; H, 10.21; S, 11.59. Found: C, 78.23; H, 10.21; S, 11.31.

(*E*)-1-(*p*-(Methoxyphenyl)thio)-1-dodecene (4j′): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$):δ 0.88 (t, J = 7.2 Hz, 3 H), 1.24−1.44 (m, 16 H), 2.10 (q, J = 7.2 Hz, 2 H), 3.79 (s, 3 H), 5.80 (dt, J = 14.7, 7.2 Hz, 1 H), 6.06 (dt, J = 15.0, 1.2 Hz, 1 H), 6.86 (d, J = 9.0 Hz, 2 H), 7.30 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.8, 29.2, 29.4, 29.5, 29.7, 32.0, 33.1, 55.4, 114.3, 114.6, 122.6, 131.8, 134.5, 158.7. IR (NaCl): 3047, 2927, 2853, 1593, 1493, 1462, 1287, 1245, 1176, 1101, 946, 825, 722, 639 cm^{-1}. MS (EI): *m*/*z* 306 (M^+, 100.0). Anal. Calcd for $C_{19}H_{30}OS$: C, 74.46; H, 9.87; S, 10.46. Found: C, 74.31; H, 9.64; S, 10.61.

(*E*)-1-(*p*-(Chlorophenyl)thio)-1-dodecene (4j″): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.0 Hz, 3 H), 1.21−1.37 (m, 14 H), 1.43 (br quint, J = 6.9 Hz, 2 H), 2.16 (dt, J = 7.2, 5.7 Hz, 2 H), 6.01 (dt, J = 6.3, 14.7 Hz, 1 H), 6.08 (d, J = 14.7 Hz, 1 H), 7.18−7.27 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 22.8, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 32.0, 33.2, 119.9, 128.9, 129.4, 129.6, 131.0, 138.8. IR (NaCl): 2924, 2852, 1475, 1094, 1012, 949, 814 cm^{-1}. MS (EI): *m*/*z* 310 (M^+, 100.0). Anal. Calcd for $C_{18}H_{27}ClS$: C, 69.53; H, 8.75. Found: C, 69.34; H, 8.59.

(*E*)-1-(Phenylthio)-5-methyl-1-hexene (4b): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (d, J = 8.4 Hz, 6 H), 1.32 (dt, J = 7.0, 8.7 Hz, 2 H), 1.59 (septet, J = 6.6 Hz, 1 H), 2.17 (ddt, J = 7.8, 6.6, 1.2 Hz, 2 H), 5.99 (dt, J = 6.6, 15.0 Hz, 1 H), 6.14 (dt, J = 1.2, 15.0 Hz, 1 H), 7.15−7.33 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.5, 27.6, 31.1, 38.2, 120.3, 125.9, 128.2, 128.8, 136.6, 137.9. IR (NaCl): 3026, 2955, 2868, 1584, 1478, 1439, 1384, 1368, 1090, 1025, 946, 819, 738, 690 cm^{-1}. MS (EI): *m*/*z* 206 (M^+, 100.0). Anal. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.53. Found: C, 75.29; H, 8.78; S, 15.09.

(*E*)-1-(Phenylthio)-5-chloro-1-pentene (4l): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.91 (quint, J = 6.6 Hz, 2 H), 2.34 (ddt, J = 0.9, 6.9, 7.2 Hz, 2 H), 3.57 (t, J = 6.3 Hz, 2 H), 5.90 (dt, J = 7.2, 15.0 Hz, 1 H), 6.23 (dt, J = 1.2, 15.0 Hz, 1 H), 7.18−7.34 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.2, 31.8, 44.2, 123.0, 126.3, 130.6, 131.9, 133.9, 135.8. IR (NaCl): 3020, 2958, 1716, 1583, 1478, 1440, 950, 711, 691 cm^{-1}. MS (EI): *m*/*z* 212 (M^+, 84.0). Anal. Calcd for $C_{11}H_{13}ClS$: C, 62.11; H, 6.16. Found: C, 62.32; H, 6.11.

(*E*)-1-(Phenylthio)-2-(1′-cyclohexenyl)ethene (4m): yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52−1.75 (m, 4 H), 2.15 (m, 4 H), 5.76 (br t, J = 3.3 Hz, 1 H), 6.21 (d, J = 15.6 Hz, 1 H), 6.46 (d, J = 15.3 Hz, 1 H), 7.19−7.37 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.4, 22.5, 24.6, 26.0, 117.6, 126.2, 128.8, 128.9, 130.1, 134.9, 137.4. IR (NaCl): 3024, 2929, 2860, 1673, 1580, 1476, 1439, 950, 741, 694 cm^{-1}. MS (EI): *m*/*z* 216 (M^+, 100.0). Anal. Calcd for $C_{14}H_{16}S$: C, 77.73; H, 7.45; S, 14.82. Found: C, 77.21; H, 7.27; S, 14.26.

(*E*)-4-(Phenylthio)-4-octene (4n): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 7.5 Hz, 3 H), 0.94 (t, J = 7.2 Hz, 3 H), 1.40−1.56 (m, 4 H), 2.09−2.20 (m, 4 H), 5.87 (t, J = 7.5 Hz, 1 H), 7.17−7.33 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 14.0, 21.8, 22.8, 31.3, 33.1, 126.0, 128.7, 129.7, 133.4, 135.9, 137.2. IR (NaCl): 3071, 2960, 2870, 1583, 1476, 1439, 1378, 1233, 1151, 1087, 1025, 898, 740, 691 cm^{-1}. MS (EI): *m*/*z* 220 (M^+, 100.0). Anal. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15; S, 14.55. Found: C, 76.17; H, 9.07; S, 14.44.

(*E*)-2-(Phenylthio)-2-methylstyrene (4o): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (s, 3 H), 6.68 (s, 1 H), 7.22−7.47 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.7, 126.7, 127.3, 128.2, 128.6, 129.0, 130.6, 132.0, 133.7, 138.8, 137.0. IR (NaCl): 3058, 3022, 2932, 2864, 1614, 1582, 1475, 1439, 1376, 1099, 1024, 917, 745, 693 cm^{-1}. MS (EI): *m*/*z* 226 (M^+, 100.0). Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.17. Found: C, 79.33; H, 6.02; S, 14.17.

Acknowledgment. This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (No. 09239102) from the Ministry of Education, Science and Culture of Japan. We are grateful to Dr. Koh Kidena for help in measurement of ^{1}H and ^{13}C NMR of complex **A** in the solid state. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining NMR spectra with the JEOL JNM-GSX-400 instrument, mass spectra with the JEOL JMS-DX303 instrument, and elemental analyses.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of complex **A** in the solid state. This material is available free of charge via the Internet at http://pubs.acs.org.

JA983949I