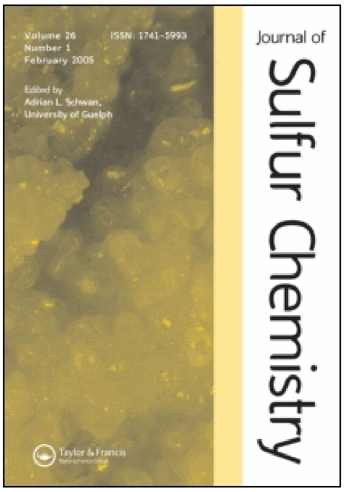

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Transition-metal-catalyzed hydrothiolation of cyclohexylallene with benzenethiol or diphenyl disulfide

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

The reaction of benzenethiol (or diphenyl disulfide) with cyclohexylallene, as a representative terminal allene, has been investigated in detail in the presence of transition metal-phosphine complexes as the catalyst. $Pd(PPh_3)_4$-catalyzed hydrothiolation of cyclohexylallene with benzenethiol in acetonitrile affords the corresponding terminal vinylic sulfide $[RCH_2C(SPh){=}CH_2 (R = {}^{c}Hex)]$ regioselectively in good yield, whereas $Pt(PPh_3)_4$-catalyzed hydrothiolation of cyclohexylallene gives the regioisomeric vinyl sulfide successfully. Similar hydrothiolation of the allene proceeds using diphenyl disulfide, instead of benzenethiol, in the presence of triphenylphosphine and water.

Keywords: hydrothiolation; allene; benzenethiol; transition metal catalyst; triphenylphosphine

1. Introduction

Allene has a cumulated diene structure with reactivity higher than those of usual C−C double bonds, and therefore allenes undergo addition of various organic molecules, affording the corresponding vinylic and/or allylic compounds (*1*). Considering the addition to allenes, regioselectivity is of great importance, because the desired allylic and/or vinylic compounds can be synthesized selectively. Recently, highly regioselective addition reactions of various heteroatom compounds to allenes have been attained in the presence of transition metal catalysts, and this addition provides straightforward access to a variety of vinylic and/or allylic heteroatom compounds (Scheme 1) (*1a, 1g, 1h, 2*).

In 1996, we developed palladium(II) acetate-catalyzed regioselective addition of benzenethiol to allenes, affording the corresponding terminal vinylic sulfides, regioselectively (*3*, *4*, *5*). In the addition of benzenethiol to terminal allenes, four types of regioisomers (**a**, **b**, **c**, and **d**) are considered formally, as shown in Scheme 2 (the first equation). Radical addition of PhSH to

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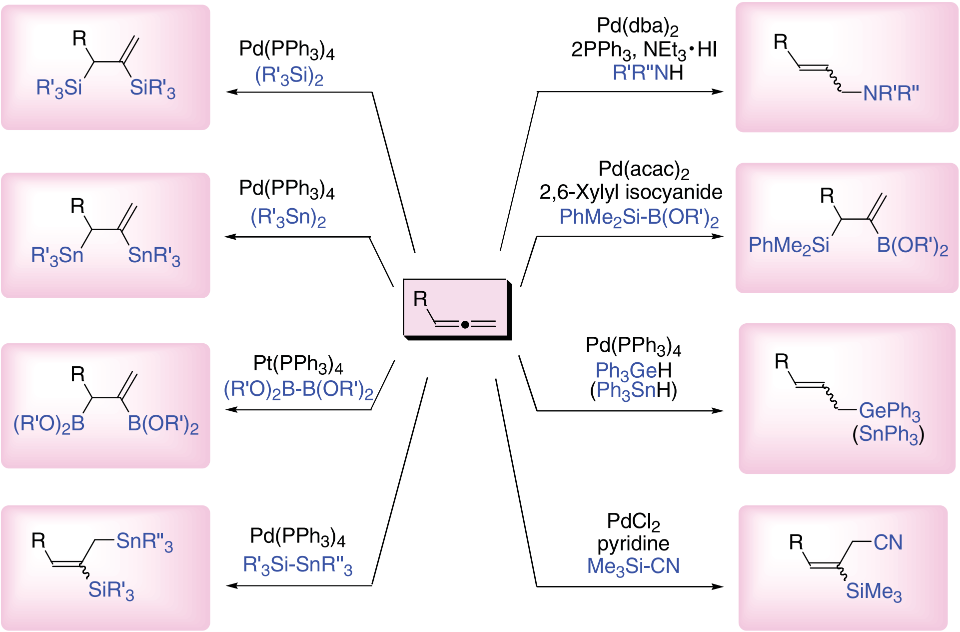
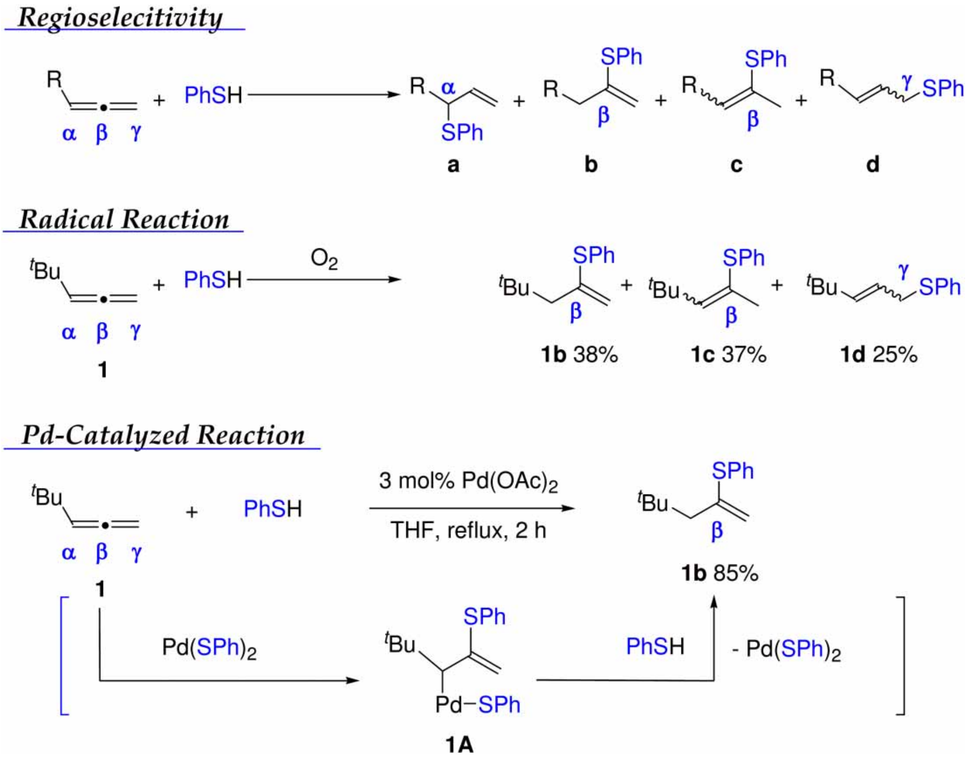


Scheme 1.



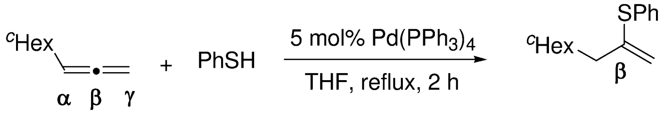
Scheme 2.

terminal allenes was reported to afford a mixture of regioisomers (**1b**, **1c**, and **1d**) (the second equation) (*6*). In contrast, the $Pd(OAc)_2$-catalyzed addition of PhSH to terminal allenes proceeds regioselectively, giving the adduct (**1b**) as a sole product (the third equation). A possible reaction pathway for the $Pd(OAc)_2$-catalyzed addition may involve the following processes: (i) ligand-exchange reaction between $Pd(OAc)_2$ and two equivalents of PhSH generates $Pd(SPh)_2$ along with two equivalents of acetic acid; (ii) thiopalladation takes place at the relatively electron-rich double bond, *i.e.* inner double bond of allenes, leading to the allylic palladium species (**1A**); (iii) protonation of the allylic palladium species (**1A**) with PhSH affords the adduct (**1b**) with regeneration of $Pd(SPh)_2$.

In place of $Pd(OAc)_2$, the use of palladium-phosphine complexes such as $Pd(PPh_3)_4$ as the catalyst usually resulted in the formation of a complex mixture involving the regioisomers of hydrothiolation products and the disulfide adducts. Indeed, the $Pd(PPh_3)_4$-catalyzed reaction of PhSH with terminal alkynes leads to a regioisomeric mixture of the thiol adducts along with the disulfide adducts (*7*, *8*). This is partly because oxidative addition of thiol to palladium(0) species generates "H–Pd–SPh" species (which induces both hydropalladation and thiopalladation of allenes), and also phosphine ligands accelerate the reductive elimination of the disulfide adducts from the palladium species (**1A**). As can be seen from Scheme 1, however, transition metal complexes bearing phosphine ligands are generally useful catalysts for the regioselective addition of heteroatom compounds to allenes. Thus, we have investigated in detail the reaction of benzenethiol (or diphenyl disulfide) with cyclohexylallene, as a representative terminal allene, in the presence of transition metal-phosphine complexes as the catalyst.

2. Results and discussion

When the reaction of cyclohexylallene with benzenethiol was conducted using tetrakis-(triphenylphosphine)palladium(0) as the catalyst in refluxing tetrahydrofuran (THF), the adduct (**2b**) was obtained in 25% yield (Equation 1), which is lower compared with that of **2b** obtained by the $Pd(OAc)_2$-catalyzed hydrothiolation (Scheme 2) (*3*). We also examined the $Pd(PPh_3)_4$-catalyzed addition of benzenethiol to *t*-butylallene (**1**) or phenylallene (**4**) in THF. In the case of *t*-butylallene (**1**), the adduct (**1b**) was obtained in very low yield, and in the case of phenylallene (**4**), the adducts $PhCH_2C(SPh){=}CH_2$ (**4b**) and $PhCH{=}C(SPh)CH_3$ (**4c**) were obtained in 23% and 3% yields, respectively.



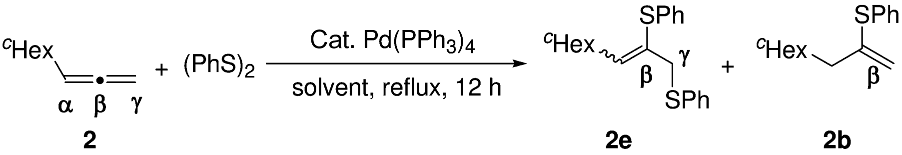
2 (1.2 equiv) **2b** 25% (1)

Very recently, we reported highly regioselective addition of diphenyl disulfide to allenes catalyzed by tetrakis(triphenylphosphine)palladium(0) (Table 1) (*9*). In this reaction, acetonitrile is the most suitable solvent, making it possible to attain the regioselective bisthiolation successfully.

Noteworthy is that the hydrothiolation product (**2b**) was formed as a byproduct in this reaction system, especially when EtOH was employed as the solvent. Thus, we were interested in conducting the $Pd(PPh_3)_4$-catalyzed regioselective hydrothiolation of allenes using not benzenethiol directly, but diphenyl disulfide.

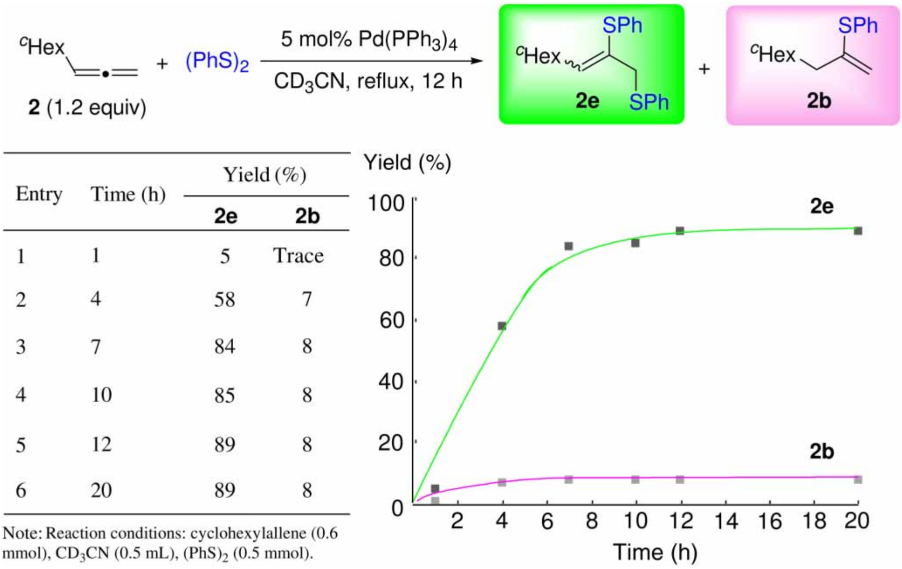
The $Pd(PPh_3)_4$-catalyzed reaction of cyclohexylallene with $(PhS)_2$ in CD_3CN was monitored by taking ^1H NMR spectra, and the results are shown in Figure 1. The yields of the bisthiolation

Table 1. Influence of solvents on the $Pd(PPh_3)_4$-catalyzed bisthiolation of cyclohexylallene.



Entry	Solvent	Temp. (°C)	Yield[a] (%) 2e	Yield[a] (%) 2b
1	THF	67	46 [$E/Z = 69/31$]	19
2	CH_3CN	82	88 [$E/Z = 91/9$]	4
3	EtOH	78	55 [$E/Z = 90/10$]	28
4	Benzene	80	69 [$E/Z = 67/23$]	7

Notes: Reaction conditions: $Pd(PPh_3)_4$ (5 mol%), solvent (0.5 mL), cyclohexylallene (0.6 mmol), $(PhS)_2$ (0.5 mmol), reflux, 12 h. [a]Determined by ^1H NMR (1,2-diphenylethane was used as an internal standard).



Entry	Time (h)	Yield (%) 2e	Yield (%) 2b
1	1	5	Trace
2	4	58	7
3	7	84	8
4	10	85	8
5	12	89	8
6	20	89	8

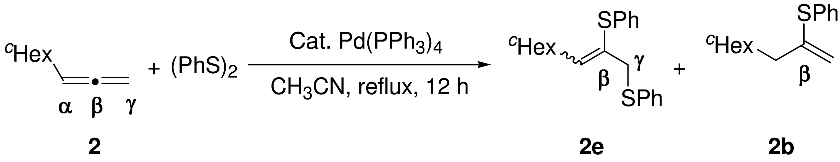
Note: Reaction conditions: cyclohexylallene (0.6 mmol), CD_3CN (0.5 mL), $(PhS)_2$ (0.5 mmol).

Figure 1.

product (**2e**) increased with the reaction time, whereas the yields of the hydrothiolation product (**2b**) increased in the initial stage, and then were constant after 4 h. These results strongly suggest that **2b** was not generated from **2e**.

As to the hydrogen source of the hydrothiolation product (**2b**), it is assumed that water existing slightly in a reaction vessel and/or reagents may work to generate **2b**. On the basis of this consideration, we examined the $Pd(PPh_3)_4$-catalyzed reaction of $(PhS)_2$ with cyclohexylallene by adding water into the reaction system. Interestingly, the addition of water inhibited the bisthiolation intensively, and instead, the corresponding terminal vinylic sulfide (**2b**) was obtained in 31% yield (Table 2, Entry 2).

Table 2. The $Pd(PPh_3)_4$-catalyzed hydrothiolation of cyclohexylallene with $(PhS)_2$ in the presence of additives.

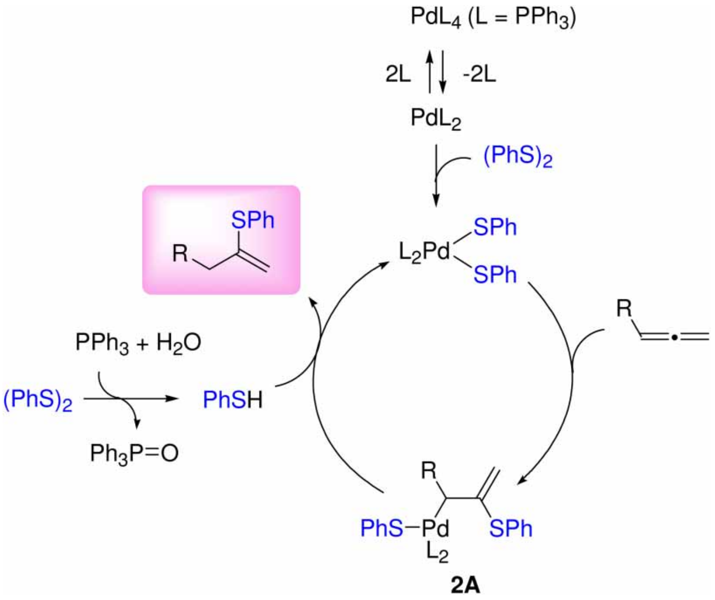


Entry	Additive	Yield[a] (%)	
		2e	**2b**
1	None	88 [$E/Z = 91/9$]	4
2	H_2O	Trace	31
3	D_2O	Trace	22[b]
4[c]	H_2O	Trace	77

Notes: Reaction conditions: $Pd(PPh_3)_4$ (5 mol%), CH_3CN (0.5 mL), cyclohexylallene (0.6 mmol), $(PhS)_2$ (0.5 mmol), additive (5 mmol), reflux, 12 h. [a]Determined by ^1H NMR (1,2-diphenylethane was used as an internal standard). [b]The yield of the deuterated product (**2b**-*d*) (D: 48 atom% of the allylic methylene). [c]PPh_3 (0.5 mmol) was added.

Furthermore, when hydrothiolation of cyclohexylallene with $(PhS)_2$ was conducted in the presence of D_2O, the deuteriothiolation product (**2b**-*d*) deuterized selectively at the allylic position (D: 48 atom% of the allylic methylene) was obtained in 22% yield (Table 2, Entry 3).

Since $Pd(PPh_3)_4$ is known to generate $Pd(PPh_3)_2$ and two equivalents of triphenylphosphine in solvent, the influence of PPh_3 on the $Pd(PPh_3)_4$-catalyzed reaction of $(PhS)_2$ with allenes was investigated. Surprisingly, the hydrothiolation of cyclohexylallene proceeded efficiently by use



Scheme 3.

of both water and triphenylphosphine as additives, affording **2b** with excellent regioselectivity (Table 2, Entry 4).

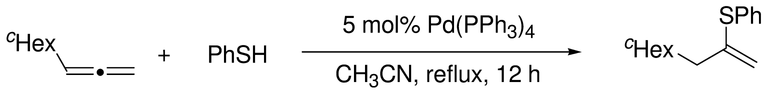
A possible pathway for the $Pd(PPh_3)_4$-catalyzed regioselective hydrothiolation with $(PhS)_2$ in the presence of water and triphenylphosphine may include the following (Scheme 3): (i) oxidative addition of $(PhS)_2$ to zerovalent palladium generating $Pd(SPh)_2$; (ii) regioselective thiopalladation at the inner double bond of the allene leading to the corresponding allylic palladium species (**2A**); (iii) protonation of the allylic palladium species (**2A**) with benzenethiol generated *in situ* by the reaction of $(PhS)_2$ with triphenylphosphine and water (*10*).

Alternatively, *in situ* formed thiol directly reacts with zerovalent palladium to generate "H–Pd–SPh" species, which may work as a key species for the hydrothiolation of allenes (Scheme 4).

Next, we examined the $Pd(PPh_3)_4$-catalyzed hydrothiolation of several allenes (0.6 mmol) using $(ArS)_2$ (0.25 mmol), water (5 mmol) and triphenylphosphine (0.25 mmol) (Table 3). Aliphatic allenes underwent regioselective hydrothiolation successfully.

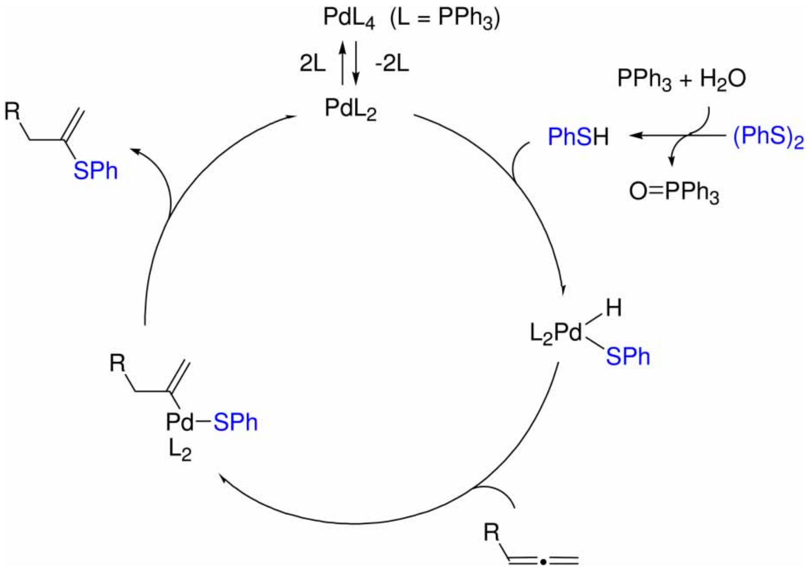
For example, di(*p*-tolyl) disulfide could be used for the regioselective hydrothiolation of cyclohexylallene to afford the product (**2b′**) in 79% yield (Table 3, Entry 2). Unfortunately, in the case of phenylallene (**4**), a mixture of regioisomers (**4b**, **4c**, and **4d**) was obtained (Table 3, Entry 5).

As mentioned above, the $Pd(PPh_3)_4$-catalyzed thiolation reactions proceed smoothly in acetonitrile as solvent. Thus, we next examined the $Pd(PPh_3)_4$-catalyzed addition of benzenethiol to cyclohexylallene in acetonitrile (Equation 2). Interestingly, the corresponding terminal vinylic sulfide (**2b**) was obtained as a sole product in 82% yield.



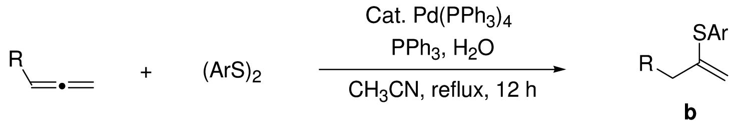
2 (0.6 mmol) (0.5 mmol) **2b** 82%

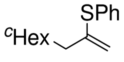
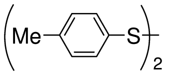
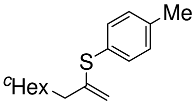
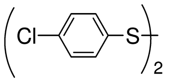
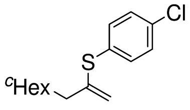
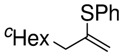
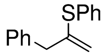
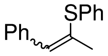
(2)



Scheme 4.

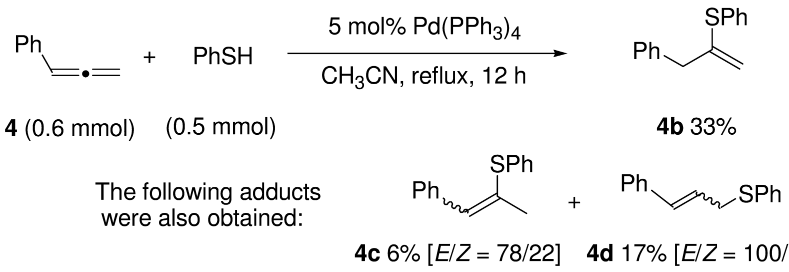
Table 3. The $Pd(PPh_3)_4$-catalyzed hydrothiolation of allenes with $(ArS)_2$ in the presence of H_2O and PPh_3.



Entry	Allene	Disulfide	Products	Yield[a] (%)
1	**2**: R = ^{c}Hex	$(PhS)_2$	 **2b**	72
2			 **2b'**	79
3			 **2b"**	38
4	**3**: R = ^{n}Hex	$(PhS)_2$	 **3b**	34
5	**4**: R = Ph	$(PhS)_2$	 **4b**	25
		The following adducts were also obtained:	 +  **4c** 6% [*E*/*Z* = 60/40] **4d** 16% [*E*/*Z* = 100/0]	

Notes: Reaction conditions: $Pd(PPh_3)_4$ (0.025 mmol), PPh_3 (0.25 mmol), CH_3CN (0.5 mL), allene (0.6 mmol), disulfide (0.25 mmol), H_2O (5 mmol), reflux, 12 h. [a]Determined by ^1H NMR (1,2-diphenylethane was used as an internal standard).

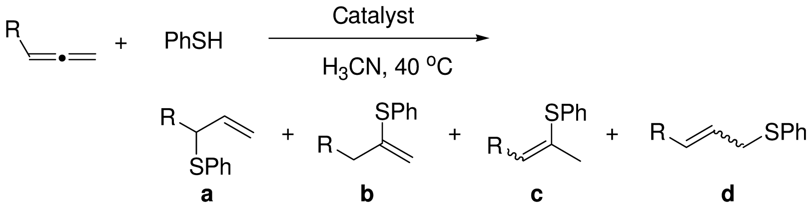
In the case of phenylallene (**4**), although a mixture of regioisomers (**4b**, **4c**, and **4d**) was obtained, the yield of **4b** was increased (Equation 3) (*cf*. Table 3, Entry 5).



(3)

In addition, we examined the reaction of cyclohexylallene with benzenethiol in acetonitrile by using $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$ as representative transition metal-phosphine complexes (Table 4).

Table 4. Hydrothiolation of allenes with PhSH using $RhCl(PPh_3)_3$ or $Pt(PPh_3)_4$.



			Yield[a] (%)			
Entry	Catalyst	Allene	a	b	c	d
1	$RhCl(PPh_3)_3$	**2**: R = ^{c}Hex	18	18	40	2
2[b]	$Pt(PPh_3)_4$	**2**: R = ^{c}Hex	n.d.	3	58	n.d.
3[b]	$Pt(PPh_3)_4$	**4**: R = Ph	n.d.	1	35	n.d.

Notes: Reaction conditions: catalyst (3 mol%), CH_3CN (1.0 mL), allene (1.0 mmol), PhSH (1.0 mmol), 40 °C, 20 h. [a]Determined by ^1H NMR (dibenzyl was used as an internal standard). [b]36 h. n.d., Not detected.

The $RhCl(PPh_3)_3$-catalyzed reaction resulted in the formation of a mixture of regioisomers (**2a**, **2b**, **2c**, and **2d**) (Table 4, Entry 1). When the reaction was conducted using $Pt(PPh_3)_4$ as the catalyst, the different regioselectivity was observed, affording **2c** or **4c** with high regioselectivity (Table 4, Entries 2, 3) (*cf.* Equations 2 and 3). These results suggest that the regioselectivity of the hydrothiolation can be controlled by the selection of catalysts, $Pd(PPh_3)_4$ or $Pt(PPh_3)_4$.

3. Conclusion

We have developed hydrothiolation of cyclohexylallene with benzenethiol (or diphenyl disulfide) in the presence of transition metal-phosphine complexes as the catalyst. By using acetonitrile as solvent, the $Pd(PPh_3)_4$-catalyzed hydrothiolation of cyclohexylallene affords the corresponding terminal vinylic sulfide (**2b**) regioselectively in good yield. In addition, it has been revealed that switching the catalyst from $Pd(PPh_3)_4$ to $Pt(PPh_3)_4$ leads to the different regioselectivity.

4. Experimental

All manipulations were performed under nitrogen atmosphere. Tetrahydrofuran and ethanol were distilled from sodium. Benzene was used after distillation from Drynap. Acetonitrile was dried by distillation from calcium hydride. Allenes **1** (*1d*), **2** (*1e*), **3** (*1e, 11*), and **4** (*1e, 11*) were prepared according to the literature methods. Benzenethiol was used after distillation. Other reagents were commercially available and used as received.

^1H NMR spectra were recorded on a JNM-LA400/WB (400 MHz) spectrometer using $CDCl_3$ as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra were taken on a JNM-LA400/WB (100 MHz) spectrometer 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. Purification was performed by preparative TLC (silica gel, hexane–EtOAc as an eluent).

4.1. *General procedure for the $Pd(PPh_3)_4$-catalyzed hydrothiolation of allenes with diphenyl disulfide*

To a mixture of cyclohexylallene (0.6 mmol), PPh_3 (0.25 mmol), and $Pd(PPh_3)_4$ (0.025 mmol) in CH_3CN (0.5 ml) were added disulfide (0.25 mmol) and water (5 mmol) under N_2 atmosphere. The resulting mixture was stirred magnetically for 12 h with heating at refluxing temperature (*e.g.* CH_3CN; 82 °C). After the reaction was complete, the reaction mixture was passed through a Celite pad, which was washed with diethyl ether. The combined solution was concentrated under reduced pressure. The yield of a product (**2b**) (*3*) was confirmed by ^{1}H NMR spectroscopy (1,2-diphenylethane was used as an internal standard). The purification of the products was performed by preparative TLC on silica gel using hexane/EtOAc = 9:1 as an eluent.

4.2. *General procedure for the transition metal-phosphine complexes-catalyzed hydrothiolation of allenes with benzenethiol in acetonitrile*

To a mixture of cyclohexylallene (0.6 mmol), $Pd(PPh_3)_4$ (0.025 mmol) in CH_3CN (0.5 ml) was added benzenethiol (0.5 mmol) under N_2 atmosphere. The resulting mixture was stirred magnetically for 12 h with heating at refluxing temperature (*e.g.* CH_3CN; 82 °C). After the reaction was complete, the reaction mixture was passed through a Celite pad, which was washed with diethyl ether. The combined solution was concentrated under reduced pressure. The yield of a product (**2b**) (*3*) was confirmed by ^{1}H NMR spectroscopy (1,2-diphenylethane was used as an internal standard). The purification of the product was performed by preparative TLC on silica gel using hexane/EtOAc = 9:1 as an eluent.

Acknowledgements

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