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Letters

A highly regioselective bisselenation of allenes with diphenyl diselenide catalyzed by tetrakis(triphenylphosphine)palladium(0)

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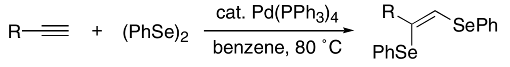
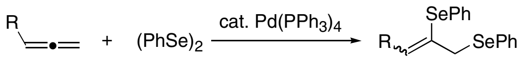
Abstract—Tetrakis(triphenylphosphine)palladium(0) acts as an effective catalyst for highly regioselective bisselenation of allenes with diphenyl diselenide.

Very recently, the transition-metal-catalyzed reactions of organosulfur compounds have been growing, and highly selective transformations of organosulfur compounds have been developed by using transition metal catalysts.[1] In contrast, examples of transition-metal-catalyzed reactions of organoselenium compounds are still rare,[2] because organoselenium compounds bind transition metal catalysts much more strongly compared with organosulfur compounds, and make the catalytic reactions ineffective. In 1991, we have found that the palladium-catalyzed addition of diphenyl diselenide to alkynes gives the corresponding vicinal diselenoalkenes in good yields (Eq. 1).[3] However, only alkynes can be employed as substrates for this bisselenation.



(1)

On the other hand, a number of transition-metal-catalyzed addition reactions of compounds bearing a heteroatom–heteroatom linkage to allenes have been investigated hitherto.[4] Contrary to this, the corresponding addition reactions of group 16 heteroatom compounds to allenes have never been reported to the best of our knowledge. In order to develop the bisselenation of carbon–carbon double bonds, much effort has been devoted and finally we have disclosed that allenes as activated carbon–carbon double bond compounds undergo the palladium-catalyzed bisselenation successfully (Eq. 2).



(2)

Table 1 summarizes the results of the palladium-catalyzed bisselenation of cyclohexylallene (**1a**) in various solvents. Although benzene is the best solvent for the palladium-catalyzed bisselenation of alkynes, the bisselenation of **1a** in benzene was sluggish (entry 1). Ethereal solvent like THF and halogenated solvent like 1,2-dichloroethane were ineffective for the desired bisselenation (entries 2 and 3). Polar solvents, especially acetonitrile, worked as an excellent solvent, providing the corresponding bisselenation product in high to excellent yields (entries 4 and 5). In this bisselenation, the molar ratio of **1a** and $(PhSe)_2$ is important: the use of slightly excess amounts of **1a** led to the formation of **2a** in high yield (entries 5–7).

Table 2 summarizes the results of the bisselenation using some other catalysts. In contrast to the zero-valent palladium complex (entry 1), divalent palladium complexes such as $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2$ exhibited lower catalytic activity toward the bisselenation of **1a** (entries 2 and 3). Recently, we have found the combination of $Pd(OAc)_2$ and pyridine leads to the highly regioselective hydroselenation of alkynes with benzeneselenol.[5] However, the $Pd(OAc)_2$–pyridine system was ineffective for this bisselenation of **1a** (entry 4). The attempted bisselenation using Wilkinson's catalyst resulted in the

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Keywords: Bisselenation; Allenes; Diphenyl diselenide; Tetrakis(triphenylphosphine)palladium(0).

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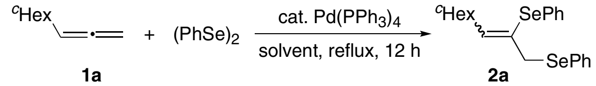
Table 1. Influence of solvents on palladium-catalyzed bisselenation



1a **2a**

Entry	Solvent	Temp. (°C)	Yield[a] (%)	[*E*/*Z*]
1	Benzene	80	14	[36/64]
2	THF	69	9	[44/56]
3	$ClCH_2CH_2Cl$	83	36	[69/31]
4	Pyridine	115	70	[31/69]
5	CH_3CN	82	96 (96)	[93/7]
6[b]	CH_3CN	82	65	[75/25]
7[c]	CH_3CN	82	61	[75/25]

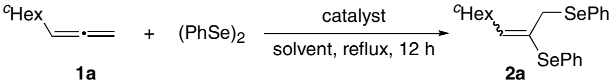
Reaction conditions: $Pd(PPh_3)_4$ (5 mol %), **1a** (0.6 mmol), solvent (0.5 mL), $(PhSe)_2$ (0.5 mmol), 12 h.

[a] ^1H NMR (isolated) yield.

[b] Allene **1a** (0.5 mmol).

[c] Allene **1a** (0.5 mmol), $(PhSe)_2$ (0.6 mmol).

Table 2. Transition-metal-catalyzed bisselenation of cyclohexylallene



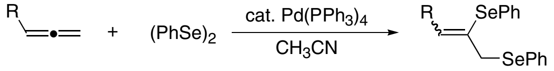
1a **2a**

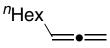
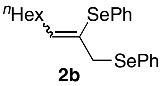
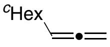
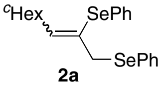
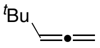
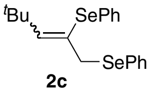
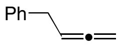
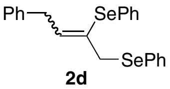
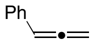
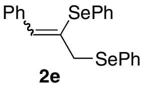
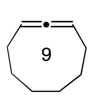
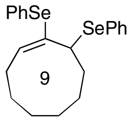
Entry	Catalyst	Solvent	Temp. (°C)	Yield[a] (%)	[*E*/*Z*]
1	$Pd(PPh_3)_4$	CH_3CN	82	96	[93/7]
2	$PdCl_2(PPh_3)_2$	CH_3CN	82	36	[53/47]
3	$Pd(OAc)_2$	CH_3CN	82	20	[60/40]
4	$Pd(OAc)_2$	Pyridine	115	Trace	
5	$RhCl(PPh_3)_3$	CH_3CN	82	A complex mixture	
6	$Pt(PPh_3)_4$	CH_3CN	82	37	[41/59]
7	No catalyst	CH_3CN	82	No reaction	

Reaction conditions: catalyst (5 mol %), **1a** (0.6 mmol), solvent (0.5 mL), $(PhSe)_2$ (0.5 mmol), 12 h.

[a] ^1H NMR yield.

Table 3. Palladium-catalyzed bisselenation of allenes with $(PhSe)_2$



Entry	Substrate	Product	Yield[a] (%)	[*E*/*Z*]
1	 **1b**	 **2b**	72[b]	[49/51]
2	 **1a**	 **2a**	96	[93/7]
3	 **1c**	 **2c**	No reaction	
4	 **1d**	 **2d**	67[c]	[41/59]
5	 **1e**	 **2e**	67[b]	[49/51]
6	 **1f**	 **2f**	81	[100/0]

Reaction conditions: $Pd(PPh_3)_4$ (5 mol %), allene (0.6 mmol), CH_3CN (0.5 mL), $(PhSe)_2$ (0.5 mmol), 82 °C, 12 h.

[a] Isolated yield.

[b] ^1H NMR yield.

[c] $Ph(CH_2)_2(PhSe)C{=}CHSePh$ was obtained in 7% yield as a byproduct.

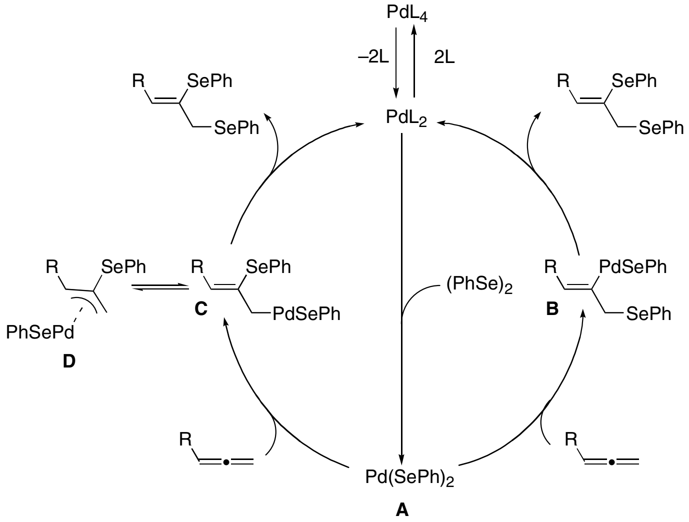
formation of a complex mixture (entry 5), whereas platinum(0) catalyst indicated moderate catalytic activity toward the desired bisselenation of **1a** (entry 6). In the absence of the catalyst, no reaction took place at all under identical conditions (entry 7). This fact clearly indicates that the present bisselenation of **1a** proceeds as a catalytic reaction of palladium(0).

Table 3 summarizes the results of the $Pd(PPh_3)_4$-catalyzed bisselenation of several allenes with $(PhSe)_2$. The representative procedure is as follows: to a mixture of cyclohexylallene (0.6 mmol) and $Pd(PPh_3)_4$ (0.025 mmol) in CH_3CN (0.5 mL) was added diphenyl diselenide (0.5 mmol) under N_2 atmosphere. The resulting mixture was stirred magnetically for 12 h with heating at 82 °C. After the reaction was complete, the reaction mixture was filtered through Celite, followed by washing with diethyl ether. The combined filtrate was concentrated under the reduced pressure, and the purification of the product was performed upon preparative TLC on silica gel using hexane/AcOEt = 100:0 to 96:4 as an eluent.[6,7]

Primary and secondary alkyl substituted allenes (**1b** and **1a**) underwent regioselective bisselenation with $(PhSe)_2$ successfully (entries 1 and 2), whereas no reaction was observed with tertiary alkyl substituted allene (**1c**), most probably due to the bulkiness of the tertiary butyl group of **1c** (entry 3). Similar conditions could be employed with benzyl and phenyl substituted allenes (**1d** and **1e**) (entries 4 and 5). In the case of benzylallene (**1d**), small amounts of the double bond isomerized byproduct was obtained exceptionally (see footnote c). Internal allene (**1f**) also underwent the desired bisselenation efficiently (entry 6).

The stereoselectivity and applicable substrates are similar to those observed in the previously reported photoinitiated bisselenation of allenes with $(PhSe)_2$ by a radical mechanism.[7] However, this transition-metal-catalyzed bisselenation involves the formation of organopalladium intermediate, which can be utilized for further useful transformations such as carbonylation with carbon monoxide (vide post).

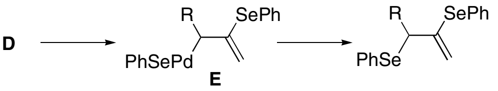
Scheme 1 shows two possible reaction pathways, which includes the following: (1) $(PhSe)_2$ adds oxidatively to the low-valent palladium(0) complex, that is, $Pd(PPh_3)_2$,



Scheme 1. Possible pathways for bisselenation of allenes with $(PhSe)_2$.

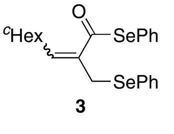
to generate an active catalyst (**A**); (2) allene coordinates to the palladium species (**A**) and then selenopalladation of allene takes place at the terminal carbon–carbon double bonds to form either vinylpalladium intermediate (**B**) or σ-allylpalladium intermediate (**C**); (3) reductive elimination of the bisselenation product with regeneration of the catalyst.

In this scheme, if **C** is in equilibrium with π-allylpalladium intermediate (**D**), **D** may generate σ-allylpalladium intermediate (**E**) to provide the corresponding regioisomeric bisselenation product (Eq. 3). However, no formation of the bisselenation product at the inner carbon–carbon double bond of allene suggests that this bisselenation of allenes does not involve the formation of allylpalladium species such as **C**, **D**, and **E**.[8]

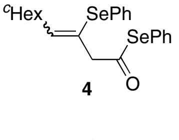


(3)

To clarify the reaction pathway, the present bisselenation of **1a** was conducted under similar reaction conditions in the presence of carbon monoxide (30 atm). The resulting reaction mixture involves the formation of a carbonylating product (**3**, 37%) along with the bisselenation product (**2a**, 4%). However, the product (**4**) derived from the carbonylation at the terminal carbon of **1a** was not obtained at all.



3



4

This observation strongly suggests the intermediacy of vinylpalladium species (**B**). It should be noted that this result is different from the addition reactions of other compounds bearing a heteroatom–heteroatom linkage to allenes, in which the corresponding π-allylpalladium intermediates are formed selectively.

In summary, we have developed the highly selective palladium-catalyzed bisselenation of allenes with diphenyl diselenide. The transition-metal-catalyzed reaction of allenes with $(PhSe)_2$ under the pressure of CO is now under investigation in detail.

References and notes

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4. For the transition-metal-catalyzed addition reactions of heteroatom compounds bearing a heteroatom–heteroatom bond to allenes, see: (a) B–B bond: Yang, F.-Y.; Cheng, C.-H. *J. Am. Chem. Soc.* **2001**, *123*, 761–762; (b) B–Si bond: Suginome, M.; Ohmori, Y.; Ito, Y. *J. Organomet. Chem.* **2000**, *611*, 403–413; (c) Si–Si bond: Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inose, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *225*, 343–356; (d) Si–Sn bond: Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354–355; (e) Sn–Sn bond: Mitchell, T. N.; Kwetkat, K.; Rutschow, D.; Schneider, U. *Tetrahedron* **1989**, *45*, 969–978.
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6. For representative spectral and analytical data, see for example: **2f**: [*E*-isomer] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09–1.23 (m, 1H), 1.37–1.69 (m, 7H), 1.81–1.93 (m, 1H), 1.97–2.08 (m, 2H), 2.20–2.27 (m, 1H), 4.51–4.61 (br m, 1H), 5.65 (t, 1H, $J = 8.8$ Hz), 7.25–7.30 (m, 6H), 7.55–7.63 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.09, 26.00, 26.24, 27.65, 29.02, 33.81, 47.50 (CH–SePh), 127.33, 127.83, 128.85, 129.09, 130.46, 130.49, 134.01, 134.46 (=C–SePh), 135.64 (CH=); IR (KBr) 3050–3000, 2925, 2853, 1580, 1485, 1440, 840, 735, 690 cm^{-1}; MS, $m/z = 436$ (M^+, 22). Anal. Calcd for $C_{21}H_{24}Se_2$: C, 58.10; H, 5.53. Found: C, 58.14; H, 5.58.
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8. Alternative pathway is as follows: the reductive elimination of the bisselenation product from σ-allylpalladium intermediate (**C**) is very fast, not generating π-allylpalladium intermediate (**D**).