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Palladium-Catalyzed Hydroselenation of Allenes with Benzeneselenol

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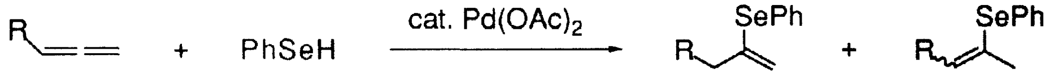
Abstract: *Palladium(II) acetate ($Pd(OAc)_2$) catalyzes the addition of benzeneselenol to allenes, providing the corresponding vinylic selenides in good yields. In contrast to the oxygen-induced radical addition of PhSeH to terminal allenes, which occurred at the terminal double bond preferentially, the present palladium-catalyzed hydroselenation to terminal allenes affords the internal adduct preferentially; thus, these two reactions are complementary to each other for the synthesis of vinylic selenides.*

Transition metal-catalyzed addition reaction of compounds bearing a main group element-hydrogen bond to carbon-carbon unsaturated bonds is an important methodology for the synthesis of main group substituted compounds, as represented by the hydrosilylation,[1] hydrostannation,[2] and hydroboration[3] of olefins, acetylenes, and conjugated dienes. However, only very limited examples of the hydrometalation of allenes have been reported hitherto, most probably due to the difficulty in controlling the regio- and stereoselectivities. The palladium-catalyzed hydrosilylation[4] and hydrogermylation[5] of allenes is reported to afford allylic silanes and germanes, respectively, with excellent regioselectivity. Very recently, the regioselectivity of the hydrostannation[5b,6] of allenes can be controlled by the selection of the catalyst: $Pd(PPh_3)_4$ is a useful catalyst for the selective formation of allylic stannanes,[6c] whereas vinylic stannnanes are obtained in the case of cat. $Pd(OH)_2/C$.[6d] We have recently disclosed that palladium(II) acetate ($Pd(OAc)_2$) catalyzes the regioselective addition of benzenethiol to allenes, providing the corresponding vinylic sulfides in good yields.[7] In extension of our interest in the transition metal-catalyzed reactions of group 16 heteroatom compounds,[8] we examined the hydroselenation of allenes catalyzed by transition metal complexes and have found that palladium(II) acetate exhibits excellent catalytic activity toward the hydroselenation of allenes with benzeneselenol, providing vinylic selenides[9] (eq 1).



(1)

1 2 3

A typical procedure for the catalytic hydroselenation of allenes is as follows: benzeneselenol (1 mmol) was added dropwise over 2 h at 55 °C to a mixture of cyclohexylallene (**1b**, 3 mmol[10]) and palladium(II) acetate (0.02 mmol, 2 mol%) under argon, and then the reaction was continued for additional 1.5 h. After

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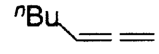
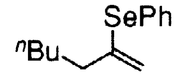
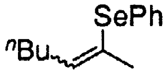
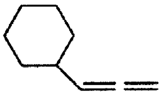
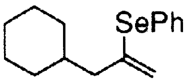
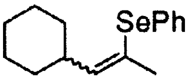
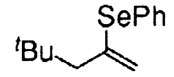
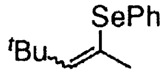
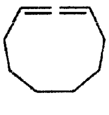
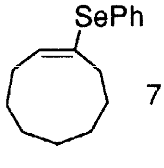
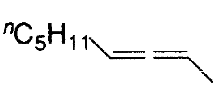
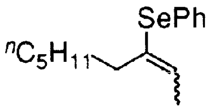
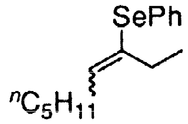
filtration of the resulting mixture through Celite, unreacted allene was removed under reduced pressure. The crude products were purified by preparative TLC (silica gel, hexane as an eluent) to afford 193 mg (69%) of 3-cyclohexyl-2-phenylseleno-1-propene (**2b**)[11] and 56 mg (20%) of 3-cyclohexyl-2-phenylseleno-2-propene (**2c**) without formation of allylic selenides (see entry 2 in Table 1).

Table 1 represents the results of the catalytic hydroselenation of allenes. Terminal allenes (**1a**-**1c**) underwent the internal addition preferentially, providing terminal vinylic selenides (**2a**-**2c**) in good yields (entries 1-3). In these reactions, the formation of allylic selenides was not detected at all. It has been reported that the radical addition of PhSeH to allenes occurs preferentially at the terminal double bond, providing the corresponding inner vinylic selenides (*e.g.*, the radical addition to **1c** provides 70% of **3c** and 8% of **2c**).[12] Accordingly, the present palladium(II) acetate-catalyzed hydroselenation and the radical reaction are complementary to each other for the synthesis of vinylic selenides. Similar conditions can be employed with internal allenes. A cyclic allene (**1d**) afforded the corresponding cyclic vinyl selenide (**2d**) as the sole product

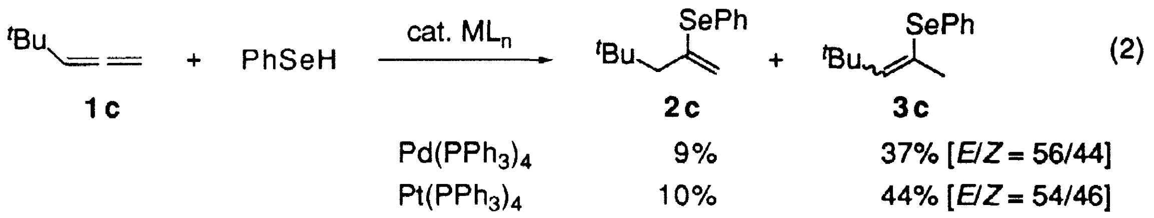
Table 1. Pd(OAc)$_2$-Catalyzed Hydroselenation of Allenes with PhSeH[a]

Entry	Allene 1	Internal Addition	Yield, %[b] [*E*/*Z*]	Terminal Addition	Yield, %[b] [*E*/*Z*]
1	 **1a**	 **2a**	63	 **3a**	16 [44/56]
2	 **1b**	 **2b**	69	 **3b**	20 [50/50]
3	 **1c**[c]	 **2c**	74	 **3c**	0
4	 **1d**	 **2d**			76 [100/0]
5	 **1e**	 **2e**	36 [71/29]	 **3e**	49 [75/25]

[a] Reaction conditions: allene (3 mmol), PhSeH (1 mmol), Pd(OAc)$_2$ (2 mol%), 55 °C, 2-5 h. [b] Isolated yield based on PhSeH. [c] Allene (5 mmol).

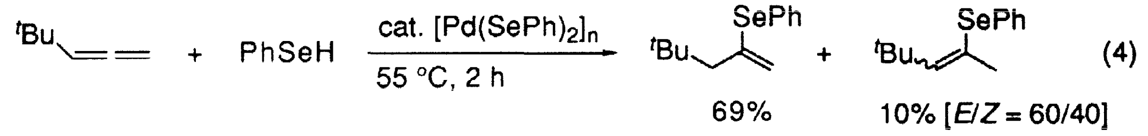
(entry 4). In the case of an asymmetrical allene (**1e**), the hydroselenation took place at both the terminal and internal double bonds, as shown in entry 5.

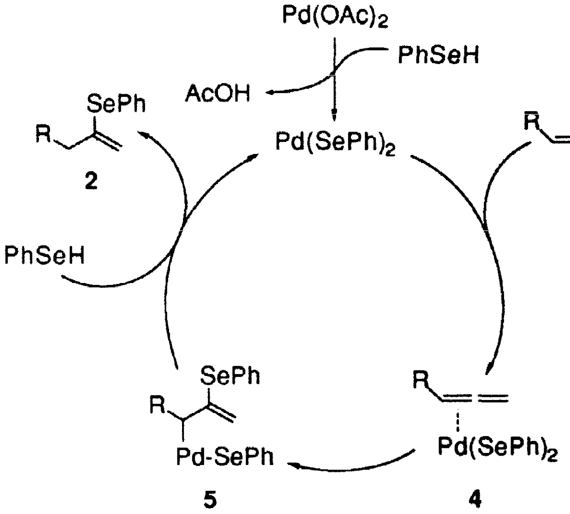
When a low-valent palladium or platinum catalyst was employed in place of $Pd(OAc)_2$ under the same conditions, vinylic selenide (**3c**) as a terminal adduct was obtained preferentially without formation of allylic selenides (eq 2).



To gain insight into the reaction pathway, the stoichiometric reaction of $Pd(OAc)_2$ with PhSeH was performed at room temperature in the presence of allene (eq 3). Immediately, a brown precipitate was formed. The IR spectrum of the precipitate (KBr: 3052, 1572, 1470, 1435, 1062, 1019, 998, 729, 685, 665 cm^{-1}) and the ^1H NMR spectrum of the resulting solution (which indicated the formation of 1.7 equiv of acetic acid) suggest that the ligand-exchange reaction took place smoothly, giving palladium selenide ($[Pd(SePh)_2]_n$). The catalytic reaction of *t*-butylallene (**1c**) with PhSeH by using the precipitate as a catalyst provided vinylic selenides in good yield, as shown in eq 4.[13]

$$\underset{}{Pd(OAc)_2} + \underset{\text{2 equiv}}{PhSeH} \xrightarrow[\text{THF, r.t.}]{} \text{" }[Pd(SePh)_2]_n\text{ "} + \underset{\text{85\% (1.7 equiv)}}{AcOH} \qquad (3)$$





Scheme 1. A Possible Reaction Path

A possible catalytic cycle is shown in Scheme 1. Initially, the ligand-exchange reaction of $Pd(OAc)_2$ with PhSeH takes place to form the palladium selenide complex, which coordinates to the double bond having higher electron density. The subsequent selenopalladation provides σ-allylic palladium intermediate (**5**), which undergoes protonation by PhSeH to give the vinylic selenide (**2**) with regeneration of the palladium selenide.

In summary, a novel palladium(II) acetate-catalyzed hydroselenation of allenes with PhSeH has been revealed. Further investigation along these lines is now in progress.

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10. As the ratio of allene/benzeneselenol is decreased, the yield of the vinylic selenide was also decreased and, instead, diphenyl diselenide was obtained as a byproduct: *e.g.*, the yield of **2c** = 56% (**1c**, 1 equiv); 61% (**1c**, 2 equiv); 69% (**1c**, 3 equiv); 79% (**1c**, 5 equiv).
11. **2b**: a yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.77-0.94 (m, 2 H), 1.07-1.34 (m, 4 H), 1.64-1.76 (m, 5 H), 2.16 (d, J = 8.40 Hz, 2 H), 5.08 (s, 1 H), 5.44 (s, 1 H), 7.27-7.33 (m, 3 H), 7.52-7.60 (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 25.2, 25.5, 31.7, 35.3, 45.2, 115.5, 126.5, 127.9, 133.7, 140.9; IR (NaCl) 3184, 3089, 2923, 1441, 738, 690 cm^{-1}; MS (EI), m/z = 280 (M$^+$, 51.5); Anal. Calcd for $C_{15}H_{20}Se$: C, 64.51; H, 7.22. Found: C, 64.22; H, 7.13.
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13. The isolated palladium selenide seems to be a polymeric structure with bridged seleno groups ($[Pd(SePh)_2]_n$) and exhibits lower catalytic activity than the real catalyst formed *in situ* in the catalytic reaction, which probably has a monomeric structure.