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Rhodium-Catalyzed Highly Stereoselective Hydroselenation of Internal Alkynes Bearing an Electron-withdrawing Group

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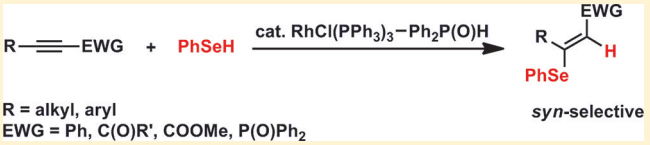
Supporting Information

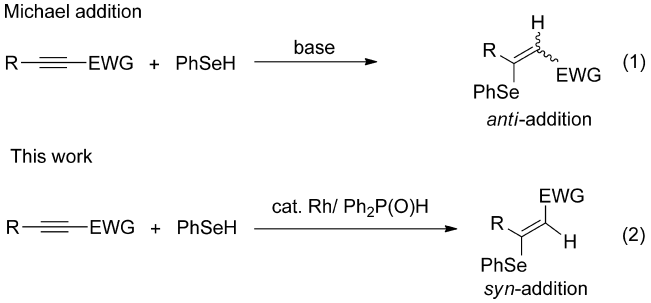
ABSTRACT: Rhodium-catalyzed highly regio- and stereoselective hydroselenation of internal alkynes bearing an electron-withdrawing group took place to give (*E*)-vinyl selenides in good yields. The excellent *syn* stereoselectivity of this rhodium-catalyzed hydroselenation is of great importance in terms of complementing the previously reported hydroselenation of alkynes.



INTRODUCTION

Organoselenium compounds are widely used as synthetic intermediates and biologically active compounds.[1] Among them, vinyl selenides are employed as synthetic equivalents of vinyl groups as well as carbonyl groups, because they can be easily converted to a variety of vinyl derivatives.[2] Addition of selenols to alkynes is one of the most straightforward methods for synthesis of vinyl selenides.[3] It has been reported that hydroselenation of alkynes proceeds via ionic pathways,[4] radical pathways,[4c,d,5] or transition-metal-catalyzed pathways.[6] It is important to control regio- and stereoselectivities of hydroselenation of alkynes, especially internal alkynes. In general, ionic additions of selenols to internal alkynes give *anti*-adducts preferentially (Scheme 1, eq 1).[4] Although transition-metal-catalyzed reactions often exhibit excellent selectivity, only very limited examples of transition-metal-catalyzed hydroselenations of internal alkynes have been reported.[7] Herein we report a highly regio- and stereoselective hydroselenation of selenols to internal alkynes with electron-withdrawing groups by using a novel $RhCl(PPh_3)_3$-$Ph_2P(O)H$ catalytic system. This hydroselenation exhibits excellent *syn*-selectivity (Scheme 1, eq 2).

Scheme 1



RESULTS AND DISCUSSION

First, we investigated the hydroselenation of 1-phosphinyl-1-octyne with benzeneselenol varying the catalysts under several conditions (Table 1). When the hydroselenation was conducted in the absence of both transition metal catalyst and additive, small amounts of Michael-type adduct were obtained with low stereoselectivity (entry 1). Addition of Et_3N increased the yield of the Michael-type adduct, but the stereoselectivity was still not improved (entry 2). Next, we attempted the hydroselenation using several palladium catalysts, but the hydroselenation did not proceed (entries 4, 6, and 7). However, Wilkinson's catalyst exhibited excellent catalytic activity toward the regio- and stereoselective hydroselenation (entry 8). Interestingly, Wilkinson's catalyst with a catalytic amount of $Ph_2P(O)H$ attained high yield and excellent selectivity, as shown in entry 10.

Table 2 represents the results of $RhCl(PPh_3)_3$-catalyzed hydroselenation of several internal alkynes. Hydroselenation of internal alkynes bearing phenyl, ester, or carbonyl groups proceeded successfully, and the corresponding (*E*)-alkenyl selenides were obtained stereoselectively in good to excellent yields (entries 1−5). Moreover, several phosphinyl-substituted internal alkynes underwent hydroselenation, and both phosphinyl- and seleno-substituted alkenes **3g** and **3h** were obtained with excellent regio- and stereoselectivities (entries 7 and 8).[8,9] In this system, curiously, hydrophosphinylation of alkynes did not take place at all. In the case of terminal alkynes such as 1-dodecyne, unfortunately, selective hydroselenation did not take place successfully under the present conditions. This reaction afforded a complex mixture involving Markovnikov adduct ($^nC_{10}H_{21}$-C(SePh)=CH_2, 31%) as a major adduct.

To gain insight into the role of $Ph_2P(O)H$, we monitored the reaction of PhSeH with $Ph_2P(O)H$ (δ 18.0 ppm, in C_6D_6) by ^{31}P NMR. When PhSeH was mixed with $Ph_2P(O)H$ in the presence of $RhCl(PPh_3)_3$ catalyst in C_6D_6, the formation of

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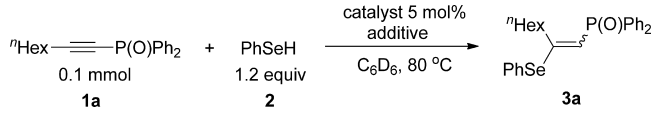
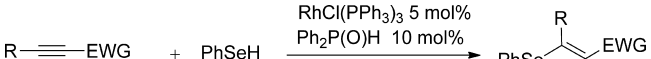
Table 1. Optimization of Hydroselenation of 1-Phosphinyl-1-octyne

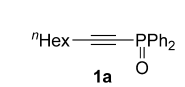
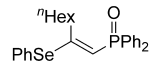
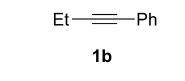
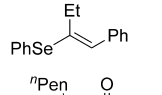
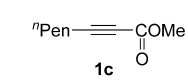
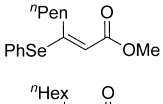
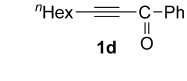
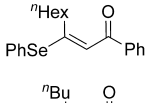
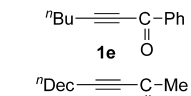
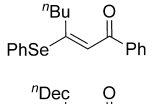
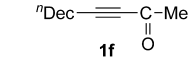
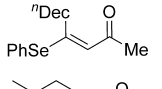
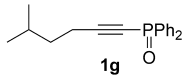
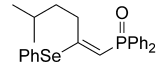
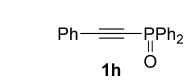
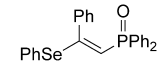


entry	catalyst	additive	time (h)	yield[a]
1	none	none	2	17% (*E*/*Z* = 59/41)
2	none	Et_3N 3 equiv	2	70% (*E*/*Z* = 40/60)
3	none	$Ph_2P(O)H$ 10 mol%	2	39% (*E*/*Z* = 28/72)
4	$PdCl_2(PPh_3)_2$	none	15	trace
5	$PdCl_2(PPh_3)_2$	Et_3N 3 equiv	2	70% (*E*/*Z* = 44/56)
6	$Pd(PPh_3)_4$	none	15	0%
7	$PdCl_2(cod)_2$	none	15	0%
8	$RhCl(PPh_3)_3$	none	2	46% (*E*/*Z* = 100/0)
9	$RhCl(PPh_3)_3$	Et_3N 3 equiv	15	8% (*E*/*Z* = 100/0)
10	$RhCl(PPh_3)_3$	$Ph_2P(O)H$ 10 mol%	2	84% (*E*/*Z* = 100/0)

[a]Determined by ^1H NMR.

Table 2. Hydroselenation of Internal Alkynes Bearing an Electron-Withdrawing Group



entry	internal alkyne	product		yield[a]
1			**3a**	84%[b] (*E*/*Z* = 100/0)
2			**3b**	54% (*E*/*Z* = 98/2)
3			**3c**	71% (*E*/*Z* = 100/0)
4			**3d**	94%[b] (*E*/*Z* = 89/11)
5			**3e**	85%[b] (*E*/*Z* = 93/7)
6			**3f**	50%[b] (*E*/*Z* = 87/13)
7			**3g**	95%[b] (*E*/*Z* = 100/0)
8			**3h**	45%[b] (*E*/*Z* = 100/0)

[a]Determined by ^1H NMR. [b]Isolated yield.

$Ph_2P(O)SePh$ (**4**) was observed (δ 37.3 ppm) (eq 3).[10] Although $Ph_2P(O)H$ is known to behave as a bidentate ligand,[11] in this hydroselenation, $Ph_2P(O)H$ preferentially converts to $Ph_2P(O)SePh$, which plays an important role in this system.

$$\underset{0.3\ \text{mmol}}{\text{PhSeH}} + \underset{1.0\ \text{equiv}}{Ph_2P(O)H} \xrightarrow[C_6D_6,\ 80\ ^\circ\text{C},\ 2\ \text{h}]{RhCl(PPh_3)_3\ 5\ \text{mol}\%} \underset{97\%}{\underset{4}{Ph_2P(O)SePh}} + H_2 \qquad (3)$$

On the other hand, PhSeH can be converted to $(PhSe)_2$ in the presence of a transition-metal catalyst. Ananikov and Beletskaya et al. have clarified the mechanism of the hydroselenation of terminal alkynes with PhSeH in the presence of Pd or Pt catalysts.[6b] In the literature, it is described that dehydrogenative coupling of PhSeH occurred to generate $(PhSe)_2$ in the system (Scheme 2, eq 4). We investigated the reaction of PhSeH in the presence of a catalytic amount of $RhCl(PPh_3)_3$ (eq 5). In a similar way, a dehydrogenative coupling reaction of PhSeH took place smoothly to afford $(PhSe)_2$ with evolution of H_2.[12] In sharp contrast, in the copresence of catalytic amounts of $RhCl(PPh_3)_3$ and $Ph_2P(O)H$, most PhSeH was unchanged except for the formation of $Ph_2P(O)SePh$ from PhSeH and $Ph_2P(O)H$ (eq 6). This clearly indicates that $Ph_2P(O)SePh$ suppresses Rh-catalyzed dehydrogenative coupling of PhSeH. When $(PhSe)_2$ and $Ph_2P(O)H$ were mixed, $Ph_2P(O)SePh$ and PhSeH were immediately formed (eq 7). We assume that this process results in depression of side reactions. Indeed, when $(PhSe)_2$ and an equimolar amount of $Ph_2P(O)H$ were employed for the Rh-catalyzed reaction of alkynes such as **1a**, hydroselenation took place successfully with excellent regio- and stereoselectivities (eq 8).

On the basis of these mechanistic experiments, a possible reaction pathway is proposed, as shown in Scheme 3. In the present $RhCl(PPh_3)_3$-$Ph_2P(O)H$ system, PhSeH reacts immediately with $Ph_2P(O)H$ to form $Ph_2P(O)SePh$ (**4**), which adds oxidatively to Rh(I) species to generate rhodium intermediate **5**. This species **5** adds to an alkyne to give vinylrhodium intermediate **6**. The subsequent protonation of vinylrhodium intermediate **6** with PhSeH leads to *syn*-adduct **3** with regeneration of rhodium species **5**.[13,14]

■ CONCLUSION

We have developed a rhodium-catalyzed, highly regio- and stereoselective hydroselenation of internal alkynes bearing electron-withdrawing groups. It has been found that addition of a catalytic amount of $Ph_2P(O)H$ can control the desired rhodium-catalyzed hydroselenation.

■ EXPERIMENTAL SECTION

General Comments. Internal alkynes **1a**,[15] **1d**,[16] **1e**,[16] **1f**,[17] **1g**,[15] and **1h**[15] were synthesized according to the literature. Other materials were obtained as commercial supplies. Benzene was purified by distillation before use. Other materials were used without further purification. The synthetic methods of compounds **3b**[4d] and **3c**[4i] are described in the literature.

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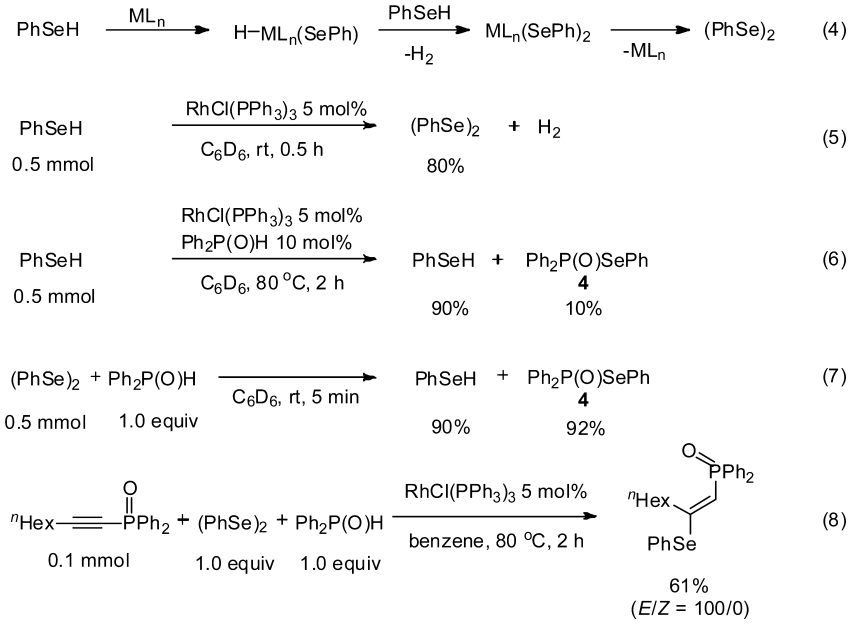
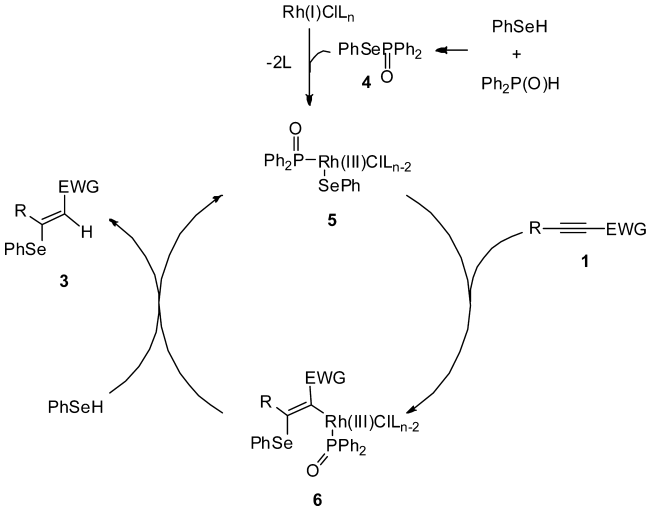
Scheme 2



Scheme 3



General Procedure for Hydroselenation of Benzeneselenol to Internal Alkynes. In a 20 mL two-necked flask equipped with a reflux condenser were placed alkyne **1** (0.1 mmol) and PhSeH (18.9 mg, 0.12 mmol) together with $RhCl(PPh_3)_3$ (4.6 mg, 0.005 mmol), $Ph_2P(O)H$ (2.0 mg, 0.01 mmol), and benzene (2 mL) under a nitrogen atmosphere. The resulting red-brown mixture was heterogeneous with a small precipitate, and it was heated at 80 °C for 2 h. During the reaction, the precipitate that came from the Rh catalyst was observed. After the reaction was complete, the mixture was filtrated through a Celite pad, the precipitate was removed by using chloroform, and then the filtrate was concentrated under reduced pressure. The crude mixture was purified by preparative TLC (eluent: hexane/AcOEt) to give vinyl selenide **3**. Compounds **3d**, **3e**, and **3f** were obtained as an *E*/*Z* mixture. Before isolation, *E*/*Z* ratios were unchanged. In the cases of **3a**, **3c**, **3g**, and **3h**, the formation of only *E*-isomers was observed in the crude mixture. The *E*/*Z* ratios were determined by ^{1}H NMR.

Spectral and Analytical Data. (*E*)-1-(Diphenylphosphinyl)-2-(phenylseleno)-1-octene (3a): pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 7.3 Hz, 3H), 1.05–1.23 (m, 6H), 1.41–1.52 (m, 2H), 2.80 (t, J = 7.8 Hz, 2H), 5.77 (d, J_{H-P} = 21.6 Hz, 1H), 7.21–7.69 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.3, 27.7, 29.0, 31.2, 40.2, 118.3 (d, J_{C-P} = 108.2 Hz), 128.4 (d, J_{C-P} = 12.4 Hz), 128.6, 128.9, 131.0 (d, J_{C-P} = 9.9 Hz), 131.4, 132.0, 133.7 (d, J_{C-P} = 105.7 Hz), 136.4, 163.3; ^{31}P NMR ($CDCl_3$) δ 22.6; HRMS (FAB) calcd for [M + H$^+$] $C_{26}H_{29}OPSe$ 469.1199, found 469.1222.

(*E*)-1-Benzoyl-2-(phenylseleno)-1-octene (3d): yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 7.1 Hz, 3H), 0.96–1.45 (m, 8H), 2.35 (t, J = 7.8 Hz, 2H), 7.24 (s, 1H), 7.34–7.52 (m, 6H), 7.69 (d, J = 6.9 Hz, 2H), 8.01 (d, J = 6.8 Hz, 2H);^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.7, 30.6, 31.4, 38.6, 118.0, 128.2, 128.7, 129.2, 130.0, 131.6, 132.3, 137.4, 138.5, 169.3, 189.0; MS (EI), m/z (%) = 372 (M$^+$, 1), 215 (M$^+$ − SePh, 19); HRMS (EI) calcd for $C_{21}H_{24}OSe$ 372.0992, found 372.0992.

(*E*)-1-Benzoyl-2-(phenylseleno)-1-hexene (3e): yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.69 (t, J = 7.3 Hz, 3H), 1.07 (sextet, J = 7.3 Hz, 2H), 1.40 (quin, J = 7.6 Hz, 2H), 2.36 (t, J = 7.8 Hz, 2H), 7.32–7.54 (m, 7H), 7.70 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.1, 32.7, 38.3, 118.0, 128.2, 128.7, 128.8, 129.16, 129.22, 132.3, 137.4, 138.5, 169.2, 189.0; MS (EI), m/z (%) = 344 (M$^+$, 2), 187 (M$^+$ − SePh, 49); HRMS (EI) calcd for $C_{19}H_{20}OSe$ 344.0679, found 344.0685.

(*E*)-4-(Phenylseleno)-tetradec-3-en-2-one (3f): pale yellow oil; ^{1}H NMR ($CDCl_3$) (*E*-isomer) δ 0.88 (t, J = 6.9 Hz, 3H), 1.21–1.34 (m, 14H), 1.56–1.64 (m, 2H), 2.19 (t, J = 7.8 Hz, 2H), 2.25 (s, 3H), 6.67 (s, 1H), 7.25–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 31.9, 37.9, 121.5, 127.8, 129.1, 135.4, 137.4, 165.7, 196.7; MS (EI), m/z (%) = 366 (M$^+$, 2), 209 (M$^+$ − SePh, 20).

(*E*)-1-(Diphenylphosphinyl)-5-methyl-2-(phenylseleno)-1-hexene (3g): yellow oil; ^{1}H NMR ($CDCl_3$) (*E*-isomer) δ 0.73 (d, J = 6.4 Hz, 6H), 1.32–1.42 (m, 3H), 2.81 (dt, $J_{H-P,H-H}$ = 1.4, 7.3 Hz, 2H), 5.81 (d, J_{H-P} = 21.5 Hz, 1H), 7.24–7.51 (m, 9H), 7.54–7.65 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 22.3, 28.1, 29.7, 34.1 (d, J_{C-P} = 7.7 Hz), 115.8 (d, J_{C-P} = 99.7 Hz), 127.6, 128.5 (d, J_{C-P} = 12.5 Hz), 129.4, 129.8, 130.8 (d, J_{C-P} = 9.6 Hz), 131.5 (d, J_{C-P} = 2.9 Hz), 134.9 (d, J_{C-P} = 104.5 Hz), 137.0, 166.1; ^{31}P NMR ($CDCl_3$) δ 19.6 ppm; HRMS (FAB) calcd for [M + H$^+$] $C_{25}H_{27}OPSe$ 455.1043, found 455.1017.

(*E*)-2-(Diphenylphosphinyl)-1-(phenylseleno)-1-phenylethene (3h): yellow oil; ^{1}H NMR ($CDCl_3$) (*E*-isomer) δ 6.12 (d, J_{H-P} = 16.0 Hz, 1H), 7.15–7.71 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 116.9 (d, J_{C-P} = 102.2 Hz), 127.6, 128.5 (d, J_{C-P} = 12.1 Hz), 128.7, 129.4, 129.8, 130.8 (d, J_{C-P} = 10.2 Hz), 130.9, 131.5, 132.2, 132.9,

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134.9 (d, J_{C-P} = 101.4 Hz), 137.2, 166.8; ^{31}P NMR ($CDCl_3$) δ 19.2 ppm; HRMS (EI) calcd for $C_{26}H_{21}OPSe$ 460.0496, found 460.0488.

Reaction of Benzeneselenol with Diphenylphosphine Oxide in the Presence of $RhCl(PPh_3)_3$ Catalyst. In an NMR tube, $Ph_2P(O)H$ (60.7 mg, 0.30 mmol), PhSeH (47.1 mg, 0.30 mmol), and $RhCl(PPh_3)_3$ (13.9 mg, 0.015 mmol) were placed with C_6D_6 (0.6 mL) under a nitrogen atmosphere. The mixture was heated at 80 °C for 2 h. During heating, evolution of gas was observed. After the reaction, the formation of $Ph_2P(O)SePh$ was determined by ^{1}H, ^{31}P, and ^{77}Se NMR spectroscopies. The yield of $Ph_2P(O)SePh$ (97%) was determined by ^{1}H NMR spectroscopy in C_6D_6 with 1,3,5-trioxane as internal standard. Spectral data of $Ph_2P(O)SePh$: ^{1}H NMR (C_6D_6) δ 6.75−6.79 (m, 3H), 6.87−6.93 (m, 6H), 7.58−7.65 (m, 2H), 7.82−7.89 (m, 4H); ^{31}P NMR (C_6D_6) δ 37.3 ppm (with 2 satellites J_{P-Se} = 372 Hz); ^{77}Se NMR δ 377 ppm (d, J_{Se-P} = 372 Hz).

Reaction of Diphenyl Diselenide with Diphenylphosphine Oxide. In an NMR tube, $Ph_2P(O)H$ (101.1 mg, 0.50 mmol), $(PhSe)_2$ (156.1 mg, 0.50 mmol), and C_6D_6 (1 mL) were placed under a nitrogen atmosphere. The mixture was stirred for 5 min at room temperature, and then NMR spectra of the crude mixture were measured. The charts of ^{31}P and ^{77}Se NMR spectroscopies indicated that $Ph_2P(O)H$ (δ 18.0 ppm in C_6D_6)[18] and $(PhSe)_2$ (δ 461 ppm in C_6D_6)[19] were consumed completely. In the crude mixture, 90% yield of PhSeH (δ 143 ppm in C_6D_6)[19] and 92% yield of $Ph_2P(O)SePh$ were formed, respectively. These yields were determined by ^{1}H NMR spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

Information about a determination of stereoselectivity for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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