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Rhodium-Catalyzed Regio- and Stereoselective 1-Seleno-2-thiolation of 1-Alkynes

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Rhodium complex $RhH(PPh_3)_4$ and 1,1′-bis(diphenylphosphino)ferrocene catalyze the regio- and stereoselective additions of diaryl disulfides and diaryl diselenides to 1-alkynes giving (*Z*)-1-arylseleno-2-arylthio-1-alkenes. The catalyst promotes the addition reaction of dibutyl disulfide and dibutyl diselenide to 1-octyne with a similar selectivity giving (*Z*)-1-butylseleno-2-butylthio-1-octene but with a lower catalytic activity. The same product is obtained with a higher yield, when excess dibutyl disulfide is used against dibutyl diselenide in the presence of $RhH(PPh_3)_4$ and 1,4-diphenylphosphinobutane.

Selenothiolation of unsaturated bonds is one of the most straightforward methods for the preparation of molecules containing both C−S and C−Se bonds, which can be interesting candidate materials for drug development.[1] This methodology will particularly be useful if convenient sulfur and selenium reagents are used and sulfur and selenium atoms are effectively discriminated, providing adducts regio- and stereoselectively. Selenothiolation of 1-alkynes using diaryl disulfides and diaryl diselenides under photoirradiation was reported by Ogawa[2] to give (*Z*)- and (*E*)-1-arylthio-2-arylselenoalkenes. The regioselectivity originated from the different reactivities of $(PhS)_2$ and $(PhSe)_2$ toward an alkenyl radical and the different reactivity of PhS and PhSe radicals toward an unsaturated bond. Only reactions of aromatic derivatives, however, were described in the study, and reactions of aliphatic derivatives were not examined. Selenothiolation of acetylene was later reported by Potapov,[3] in which an equilibrated system of disulfide/diselenide/selenosulfide was treated with acetylene under basic conditions giving (*Z*)-1-seleno-2-thioethenes as major products. The reaction, however, required a higher pressure to obtain the products with acceptable yields. The reaction of 1-alkyne was not studied here.

We previously reported the reactions of disulfides or diselenides with 1-alkynes[4] or allenes[5] catalyzed by a combination of a rhodium complex and a sulfonic acid. The reaction of 1-alkynes gave (*Z*)-1,2-bisthio-1-alkenes, while the reaction of allenes gave a mixture of (*E*)-2-thio(seleno)-1,3-dienes and (*E*)-2-thio(seleno)-2-alkenes via concomitant hydride transfer. These C−S and C−Se bond formation reactions could be applied not only to aromatic disulfides but also to aliphatic disulfides. It was also recently found that the rhodium complex system catalyzes the exchange reaction of a disulfide and a diselenide giving a selenosulfide.[6] It therefore appears interesting to determine what happens if a mixture of a disulfide and a diselenide is treated with a 1-alkyne. In principle, such a reaction can provide eight adducts: **20**, **21**, **26**, **27**, and their stereosisomers (Scheme 1). We describe here that the reaction of a 1-alkyne with a diaryl disulfide and a diaryl diselenide in the presence of $RhH(PPh_3)_4$ and 1,1′-bis(diphenylphosphino)ferrocene (dppf) predominantly gives a (*Z*)-1-arylseleno-2-arylthio-1-alkene. Reactivity and selectivity markedly change depending on the added phosphine. It is also notable that transition-metal catalysis provides a regioisomer of the photoirradiation method.[2] Reactions of aliphatic substrates were also examined.

When 1-octyne **1** was treated with di(*p*-tolyl) disulfide **2** (eq 1) and diphenyl diselenide **3** (eq 1) in the presence of $RhH(PPh_3)_4$ (5 mol %) and dppf (10 mol %) in refluxing acetone for 4 h, (*Z*)-1-phenylseleno-2-(*p*-tolylthio)-1-octene ((*Z*)-**4**) was obtained with 68% yield, which was accompanied by (*Z*)-2-phenylseleno-1-(*p*-tolylthio)-1-octene ((*Z*)-**5**) (2%), (*Z*)-1,2-bis(*p*-tolylthio)-1-octene ((*Z*)-**6**) (3%), and (*Z*)-1,2-bis(phenylseleno)-1-octene ((*Z*)-**7**) (19%) (^{1}H NMR yield) (Table 1, entry 3). No *E* isomers could be detected by ^{1}H NMR analysis of the crude product. The major compound (*Z*)-**4** could be isolated by preparative recycling reverse phase HPLC. The regio- and stereochemistries of (*Z*)-**4** were determined by NOE between the vinylic proton and the allylic methylene proton and

(1) See the following examples for the synthesis of such compounds: (a) Back, T. G.; Bethell, R. J.; Parvez, M.; Wehrli, D. *J. Org. Chem.* **1998**, *63*, 7908. (b) Hibino, M.; Koike, T.; Yoshimatsu, M. *J. Org. Chem.* **2002**, *67*, 1078. (c) Billard, T.; Langlois. B. R. *Tetrahedron* **1999**, *55*, 8065.

(2) (a) Ogawa, A.; Obayashi, R.; Ine, H.; Tsuboi, Y.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1998**, *63*, 881. (b) Ogawa, A.; Hirao, T. *Rev. Heteroat. Chem.* **1998**, *18*, 1.

(3) Potapov, V. A.; Amosova, S. V.; Zhnikin, A. R.; Sedunova, O. V.; Starkova, A. A. *Sulfur Lett.* **2001**, *24*, 251.

(4) Arisawa, M.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 763.

(5) Arisawa, M.; Suwa, A.; Fujimoto, K.; Yamaguchi, M. *Adv. Synth. Catal.* **2003**, *345*, 560.

(6) Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6624. It was later found that trifluoromethanesulfonic acid was not essential for the exchange of a disulfide and a diselenide.

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SCHEME 1

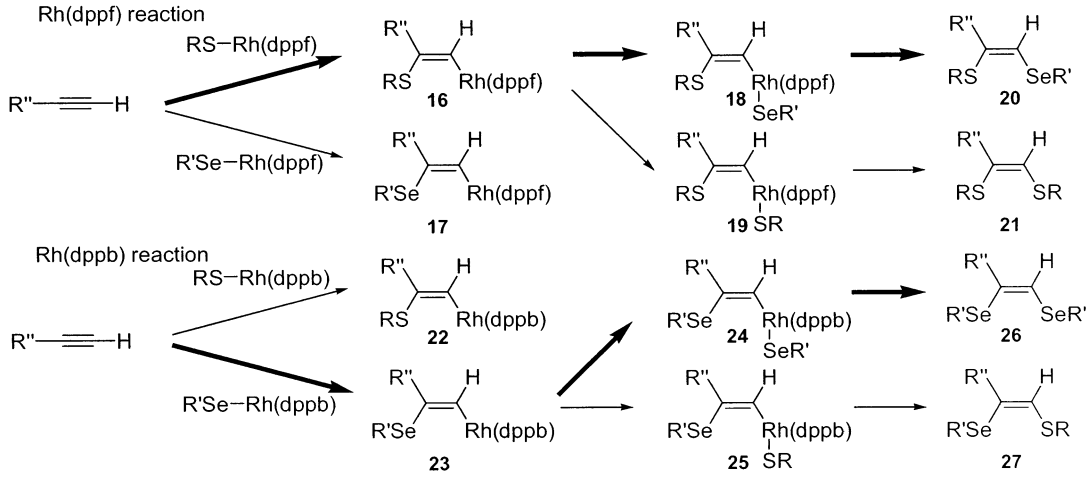
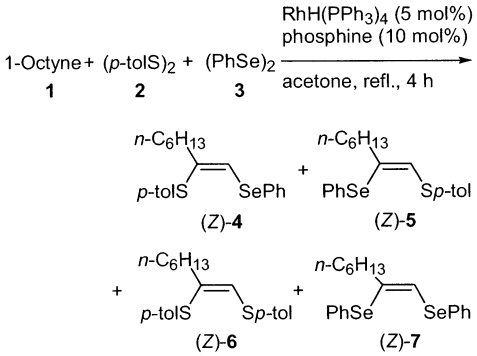


TABLE 1. Effect of Phosphine on the Addition of 2 and 3 to 1



			yield (%)[a]			
entry	phosphine	molar ratio **1**:**2**:**3**	(*Z*)-**4**	(*Z*)-**5**	(*Z*)-**6**	(*Z*)-**7**
1[b]	none	1:1:1				
2	none	1:1:1		trace	trace	
3	dppf	1:1:1	68	2	3	19
4[c]	dppf	1:1:1	30	20	19	20
5	dppf	1:1:0.5	69 (66)	trace	4	7
6	dppe	1:1:1				
7	dppp	1:1:1	9	8	4	14
8	dppb	1:1:1	28	3	1	15
9	dpppe	1:1:1		trace	trace	

[a] ^{1}H NMR yields based on acetylene. A value in parentheses is isolated yield. [b] In the absence of $RhH(PPh_3)_4$. [c] In the presence of trifluoromethanesulfonic acid (5 mol %).

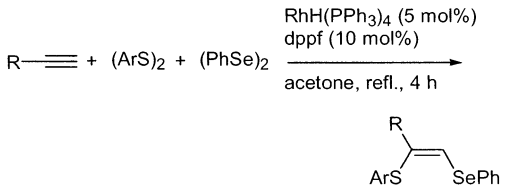
by the coupling constant ^1J ($^{13}C-^{77}Se$) = 102 Hz at the 1-carbon,[7] which was assigned by C−H COSY. The structures of (*Z*)-**6** and (*Z*)-**7** were determined according to previous reports[4,8] and that of (*Z*)-**5** by analogy with known (*Z*)-2-phenylseleno-1-phenylthio-1-octene.[2] Essentially no reaction took place in the absence of $RhH(PPh_3)_4$ (entry 1) or dppf (entry 2). When trifluoromethanesulfonic acid[6] was added, the selectivity for (*Z*)-**4** decreased (entry 4). Use of 1,3-bis(diphenylphosphino)propane (dppp) or 1,4-bis(diphenylphosphino)butane (dppb) ligand resulted in lower selectivities and yields (entries 7 and 8), and 1,2-bis(diphenylphosphino)ethane (dppe) and 1,5-bis(diphenylphosphino)pentane (dpppe) did not catalyze the reaction (entries 6 and 9). Thus, an appropriate carbon chain length between two phosphorus groups is essential. Since the amount of (*Z*)-**7** formed was higher than that of (*Z*)-**6** in the dppf reaction (entry 3), the reactivity of **3** toward **1** should be higher than that of **2** toward **1**. In accordance, when **1**, **2**, and **3** were reacted in a 1:1:0.5 ratio, the selectivity of (*Z*)-**4** (66%) increased (entry 5).

The rhodium-catalyzed selenothiolation of various 1-alkynes using diaryl disulfides and diaryl diselenides proceeded with high selectivity under these conditions, and other isomers were generally obtained with less than 10% yield (Table 2). Selectivity, however, decreased in the case of a hindered substrate *tert*-butylacetylene, and a considerable amount (25%) of 1,2-bis(phenylthio)alkene was formed as a byproduct (entry 6). Aromatic substituents of the diaryl disulfide did not largely affect the yield (entries 1, 2, and 3). Functional groups such as hydroxy (entry 7), ester (entry 8), and *tert*-butyldimethylsilyloxy (entry 9) were unaffected, and an olefin did not interfere with the addition reaction (entry 10). Atmospheric pressure acetylene was reacted with diphenyl disulfide and diphenyl diselenide **3** giving (*Z*)-1-phenylseleno-2-phenylthioethene with 51% yield, when a catalytic amount of trifluoromethanesulfonic acid was added, and the reaction was conducted in THF (entries 11 and 12). A small amount of (*Z*)-1,2-bis(phenylseleno)ethene (10%) was formed as in the reactions of 1-alkynes. An internal alkyne 4-octyne, however, did not give the addition products.

Aliphatic disulfides and diselenides exhibited similar selectivities and slightly different reactivities. Treatment of equimolar amounts of **1**, dibutyl disulfide **8**, and dibutyl diselenide **9** in the presence of $RhH(PPh_3)_4$ and dppf predominantly gave (*Z*)-1-butylseleno-2-butylthio-1-octene ((*Z*)-**10**) (33%), which was accompanied by 1,2-bis(butylseleno)-1-octene ((*Z*)-**13**) (17%) (Table 3, entry 8). The regio- and stereochemistries of (*Z*)-**10** were determined analogously with aryl substrates. The relatively low total yield was due to the inactivation of the catalyst, since **8**, **9**, and butylseleno butyl sulfide were recovered with 61% yield in a 3:2:1 ratio.[4] Increase of the amount of **8** improved the selectivity of (*Z*)-**10**, although

(7) Gulliver, D. J.; Hope, E. G.; Levason, W.; Murray, S. G.; Potter, D. M.; Marshall, G. L. *J. Chem. Soc., Perkin Trans. 2* **1984**, 429.
(8) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.

TABLE 2. Rh-Catalyzed Selenothiolation of 1-Alkynes with Aromatic Disulfides and Diphenyl Diselenides



Entry	R	Ar	Yield/% [a, b]
1	n-C_6H_{13}	p-tol	69 (66)
2		Ph	72 (68)
3		p-ClC_6H_4	79
4	n-$C_{10}H_{21}$	Ph	75 (71)
5	$Ph(CH_2)_2$	Ph	65
6[d]	t-Bu	Ph	61 (65) [e]
7	$HO(CH_2)_2$	Ph	71 (62)
8	$AcO(CH_2)_2$	Ph	78 (70)
9	t-$BuMe_2SiO(CH_2)_2$	Ph	72 (70)
10	EtO_2C, CO_2Et	Ph	73
11	H	Ph	11
12[f]		Ph	56 (51)

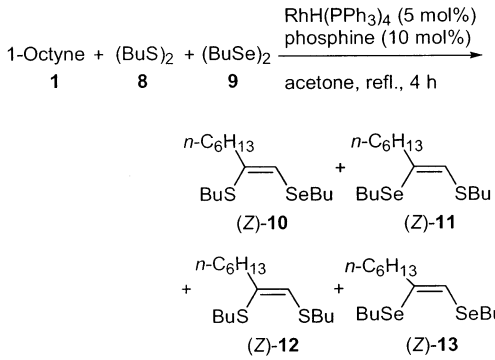
[a] See Supporting Information for the byproducts. [b] ^{1}H NMR yields based on acetylene. Values in parentheses are isolated yields. [d] The reaction was conducted at room temperature for 15 h. [e] 1,2-Bis(phenylthio)-3,3-dimethylbutene was obtained in 25% yield. [f] The reaction was conducted in the presence of CF_3SO_3H (5 mol %), $RhH(PPh_3)_4$ (10 mol %), and dppf (20 mol %) under 1 atm ethyne in THF for 12 h.

the total yield remained low (entries 9 and 10). In contrast, when equimolar amounts of **1**, **8**, and **9** were reacted in the presence of dppb, (*Z*)-**13** (42%) was obtained as a major product and (*Z*)-**10** only with 17% yield (entry 4). The yield of (*Z*)-**10**, however, increased to 56% and that of (*Z*)-**13** decreased to 17% when **8** and **9** were reacted in a 4:1 ratio (entry 6). No reaction took place in the absence of phosphine (entry 1). Ligands dppe and dpppe were not effective at all (entries 2 and 7). Thus a similar ligand effect is observed for the aliphatic substrates **8**/**9** and the aromatic substrates **2**/**3**. Bidentate diphenylphosphino ligands with an appropriate chain length between the phosphorus atoms promote the addition reactions, and use of dppf gives favorable results in terms of selectivity. It was also noted that the Rh−(dppf) catalyst is more selective than the Rh−(dppb) catalyst in the formation of (*Z*)-**10**, although the latter is more robust. Several 1-alkynes were reacted with **8** and **9** in the presence of the Rh−(dppb) catalyst to give (*Z*)-2-butylthio-1-butylseleno-1-alkenes with moderate yields, which were accompanied by approximately 20% yields of (*Z*)-1,2-bis(butylseleno)alkenes (Table 4).

The mechanism of the addition reaction is likely to involve 2-thio(seleno)-1-rhodation of 1-alkynes[9] followed by reductive elimination (Scheme 1). Since exchange of RSSR and R′SeSeR′ rapidly takes place under the conditions,[6] both RS−Rh and R′Se−Rh species should exist in the reaction mixture. It is therefore reasonably assumed, in the case of the Rh−(dppf) reaction, that the insertion of a 1-alkyne to the S−Rh(dppf) bond giving **16** is more rapid than that of the Se−Rh(dppf) bond giving **17**. The reductive elimination of the resultant selenorhodium **18** takes place more rapidly than that of thiorhodium complex **19**, and thioselenoalkene **20** is obtained. When Rh−(dppb) is used, diselenation predominates. Thus, the insertion of a 1-alkyne to the Se−Rh(dppb) bond giving **23** should be more rapid than that to the S−Rh(dppb) bond giving **22**, which is in contrast to the Rh(dppf) reaction. The reductive elimination of the Se−Rh(dppb) complex giving **26** is more rapid than that of the S−Rh(dppb) complex, which is analogous to the Rh(dppf) reaction. The phosphine ligand substantially

(9) For example: Ikeda, T.; Mizobe, Y.; Hidai, M. *Organometallics*, **2001**, *20*, 4441.

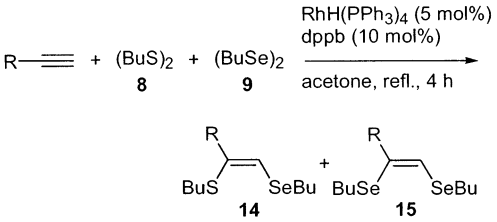
TABLE 3. Effect of Phosphine on the Addition of 8 and 9 to 1



entry	phosphine	molar ratio **1**:**8**:**9**	yield (%) (*Z*)-**10**	(*Z*)-**11**	(*Z*)-**12**	(*Z*)-**13**
1	none	1:1:1				
2	dppe	1:1:1				
3	dppp	1:1:1	14			30
4	dppb	1:1:1	17	6	trace	42
5	dppb	1:1:0.5	46	3	4	20
6	dppb	1:2:0.5	56 (53)	4	6	17
7	dpppe	1:1:1				trace
8	dppf	1:1:1	33	trace	trace	17
9	dppf	1:1:0.5	29	trace	trace	4
10	dppf	1:2:0.5	27	trace	trace	6

[a] ^{1}H NMR yields based on acetylene. A value in parentheses is isolated yield.

TABLE 4. Rh-Catalyzed Selenothiolation of 1-Alkynes with 8 and 9



entry	R	yield (%)[a] **14**	**15**
1	n-C_6H_{13}	56 (53)	17 (19)
2	n-$C_{10}H_{21}$	53	19
3	$Ph(CH_2)_2$	41	21
4	t-$BuMe_2SiO(CH_2)_2$	50 (48)	17 (17)

[a] ^{1}H NMR yields based on acetylene. Values in parentheses are isolated yield.

affects the 1-alkyne insertion to the heteroatom−rhodium complex. It should be noted that the combination of a rhodium complex and an appropriate phosphine ligand discriminates between sulfur and selenium atoms in the C−S/C−Se bond formation.

Experimental Section

(*Z*)-1-Phenylseleno-2-(*p*-tolylthio)-1-octene ((*Z*)-4) (Table 2, Entry 1). In a two-necked flask equipped with a reflux condenser were placed tetrakis(triphenylphosphine)hydride-rhodium (5 mol %, 28.8 mg), 1,1′-bis(diphenylphosphino)-ferrocene (10 mol %, 27.7 mg), di(*p*-tolyl)disulfide **2** (0.5 mmol, 123.2 mg), diphenyl diselenide **3** (0.25 mmol, 78.0 mg), and 1-octyne **1** (0.5 mmol, 55.1 mg) in acetone (2 mL) under an argon atmosphere, and the solution was heated at reflux for 4 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel giving a mixture (169.6 mg) containing (*Z*)-1-phenylseleno-2-phenylthio-1-octene (*Z*)-**4** (69%), (*Z*)-2-phenylseleno-1-phenylthio-1-octene (*Z*)-**5** (trace), (*Z*)-1,2-bis(*p*-tolylthio)-1-octene (*Z*)-**6** (4%), and (*Z*)-1,2-bis(phenylseleno)-1-octene (*Z*)-**7** (7%). The yields were determined by ^{1}H NMR ($CDCl_3$) using 1,4-dioxane as an internal standard. The major compound (*Z*)-**4** (128.4 mg, 66%) was isolated by preparative recycling reverse-phase HPLC using a Cadenza CD-C18 column (MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (3H, t, J = 6.8 Hz), 1.16−1.28 (6H, m), 1.47 (2H, quintet, J = 7.2 Hz), 2.19 (2H, t, J = 7.2 Hz), 2.33 (3H, s), 6.72 (1H, s), 7.10 (2H, d, J = 8.0 Hz), 7.23−7.33 (5H, m), 7.55 (2H, dd, J = 7.6, 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 21.2, 22.7, 28.5, 28.6, 31.6, 37.6, 126.5 ($^1J_{C-Se}$ = 102 Hz), 127.2, 129.1, 129.6, 129.8, 130.8, 131.1, 132.5, 136.8, 136.8. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 389.3. IR (neat): 3018, 2927, 2855, 1578 cm^{-1}. MS (EI) *m*/*z* 390 (M^+, 100). HRMS Calcd for $C_{21}H_{26}SSe$: 390.0920. Found: 390.0925. (*Z*)-**5** (δ 6.58) was assigned by analogy with (*Z*)-2-phenylseleno-1-phenythio-1-octene.[2] (*Z*)-**6** (δ 6.44) and (*Z*)-**7** (δ 6.92) were assigned according to literature.[4,8]

(*Z*)-1-Phenylseleno-2-phenylthioethene (Table 2, Entry 12).[3,10,11] In a two-necked flask equipped with a reflux condenser were placed tetrakis(triphenylphosphine)hydride-rhodium (10 mol %, 28.8 mg), 1,1′-bis(diphenylphosphino)-ferrocene (20 mol %, 27.7 mg), diphenyl disulfide **2** (0.25 mmol, 54.6 mg), diphenyl diselenide **3** (0.125 mmol, 39.0 mg), and trifluoromethanesulfonic acid (5 mol %, 1.1 μL) in THF (1 mL) under an acetylene atmosphere (1 atm), and the solution was heated at reflux for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel giving a mixture (50.8 mg) containing (*Z*)-1-phenylseleno-2-(phenylthio)-ethene (56%), (*Z*)-1,2-bis(phenylthio)ethene[3,4,10] (3%), and (*Z*)-1,2-bis(phenylseleno)ethene[3,7,10,11] (10%). The yields were determined by ^{1}H NMR ($CDCl_3$) using 1,4-dioxane as internal standard. The major compound (37.0 mg, 51%) was isolated by preparative recycling reverse-phase HPLC using a Cadenza CD-C18 column (MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (1H, d, J = 8.0 Hz), 6.84 (1H, d, J = 8.4 Hz), 7.23 (1H, tt, J = 7.2, 1.2 Hz), 7.26−7.34 (5H, m), 7.39 (2H, dd, J = 9.6, 1.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.0, 123.8 ($^1J_{C-Se}$ = 105 Hz), 126.8, 127.3, 129.0, 129.2, 129.3, 130.4, 132.2, 134.8. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 372.8. IR (neat): 3057, 1577, 1532 cm^{-1}. MS (EI) *m*/*z* 51 (M^+ − 241, 62), 77 (M^+ − 215, 83), 91 (M^+ − 201, 67), 109 (M^+ − 183, 75), 135 (M^+ − 157, 64), 183 (M^+ − 109, 100) 292 (M^+, 80). HRMS Calcd for $C_{14}H_{12}SSe$: 291.9825. Found: 291.9803. Anal. Calcd for $C_{14}H_{12}SSe$: C, 57.73; H, 4.15. Found: C, 58.14; H, 4.32. (*Z*)-1,2-Bis(phenylthio)ethene (δ 6.52) and (*Z*)-1,2-bis(phenylseleno)ethene (δ 7.16) were assigned according to literature.[3,4,7,10,11]

(*Z*)-1-Butylseleno-2-butylthio-1-octene ((*Z*)-16) (Table 4, Entry 1). In a two-necked flask equipped with a reflux condenser were placed tetrakis(triphenylphosphine)hydride-rhodium (5 mol %, 28.8 mg), 1,4-bis(diphenylphosphino)butane (10 mol %, 27.7 mg), dibutyl disulfide (**8**) (1.0 mmol, 178.4 mg), dibutyl diselenide (**9**) (0.25 mmol, 68.0 mg), and 1-octyne (**1**) (0.5 mmol, 55.1 mg) in acetone (2 mL) under an argon atmosphere, and the solution was heated at reflux for 4 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel giving a mixture (149.8 mg) containing (*Z*)-1-butylseleno-2-butylthio-1-octene ((*Z*)-**10**) (56%), (*Z*)-2-butylseleno-1-butylthio-1-octene ((*Z*)-**11**) (4%), (*Z*)-1,2-bis(butylthio)-1-octene ((*Z*)-**12**) (6%), and (*Z*)-1,2-bis(butylseleno)-1-octene ((*Z*)-**13**) (17%). The yields were determined by ^{1}H NMR ($CDCl_3$) using 1,4-dioxane as internal standard. The major compound (*Z*)-**10** (88.9 mg, 50%) was isolated by preparative recycling reverse-phase HPLC using Cadenza CD-C18 column (MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, J = 7.2 Hz), 0.91 (3H, t, J = 7.2 Hz), 0.92 (3H, t, J = 7.2 Hz), 1.22−1.35 (6H, m), 1.41 (2H, sextet, J = 7.6 Hz), 1.42 (2H, sextet, J = 7.6 Hz), 1.48−1.60 (4H, m), 1.69 (2H, quintet, J = 7.6 Hz), 2.25 (2H, t, J = 7.6 Hz), 2.68 (2H, t, J = 7.2 Hz), 2.69 (2H, t, J = 7.6 Hz), 6.32 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 13.8, 14.2, 22.0, 22.7, 23.0, 26.5, 28.5, 28.7, 31.4, 31.7, 32.1, 33.1, 37.5, 122.3 ($^1J_{C-Se}$ = 100 Hz), 135.5. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 257.0. IR (neat): 2956, 2927, 2857, 1574 cm^{-1}. MS (EI) *m*/*z* 43 (M^+ − 293, 100), 336 (M^+, 29). HRMS. Calcd for $C_{16}H_{32}SSe$: 336.1390. Found: 336.1370. (*Z*)-**12** (δ 6.04) and (*Z*)-**13** (δ 6.54) were assigned according to literature.[2,7] A peak at δ 6.21 was assigned to (*Z*)-**11** tentatively.

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Supporting Information Available: Spectroscopic data for the products in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034990T

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