Palladium-Catalyzed Addition and Carbonylative Addition of Diaryl Disulfides and Diselenides to Terminal Acetylenes

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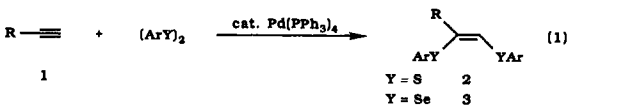
Abstract: Novel transition-metal-catalyzed reactions of disulfides and diselenides with acetylenes are described. In the presence of tetrakis(triphenylphosphine)palladium(0), [$Pd(PPh_3)_4$], the (1) of diaryl disulfides and diselenides to terminal acetylenes **1** takes place stereoselectively to give high yields of (*Z*)-1,2-bis(arylthio)-1-alkenes **2** and (*Z*)-1,2-bis(arylseleno)-1-alkenes **3**, respectively. A mechanistic proposal includes the following: (1) oxidative addition of $(ArY)_2$ [Y = S, Se] to low-valent palladium species, (2) stereoselective cis-thiopalladation or cis-selenopalladation to acetylenes to form a *cis*-vinylpalladium intermediate, and (3) reductive elimination of the product with retention of the stereochemistry. When the reaction of diaryl disulfides and diselenides with terminal acetylenes is performed under the pressure of carbon monoxide, the carbonylative addition occurs to afford (*Z*)-1,3-bis(arylthio)-2-alken-1-ones **4** and (*Z*)-1,3-bis(arylseleno)-2-alken-1-ones **5**, respectively. Carbon monoxide is regioselectively incorporated on the side of the terminal carbon of the acetylenes.

Introduction

Although organic disulfides and diselenides have been widely employed as the sources of ligands for various transition metals,[1] the transition-metal-catalyzed reactions using them as substrates have been scarcely developed.[2,3] This might be partly due to the widespread belief that a lot of chalcogen compounds work as catalyst poisons. We now wish to report our novel discovery that palladium complexes like $Pd(PPh_3)_4$ indeed catalyze the addition of diaryl disulfides and diselenides to terminal acetylenes **1**, which leads to the stereoselective formation of (*Z*)-1,2-bis(arylthio)-1-alkenes **2** and (*Z*)-1,2-bis(arylseleno)-1-alkenes **3**, respectively (eq 1).[4,5] Furthermore, the application of this reaction system to the carbonylative addition under pressurized carbon monoxide is also described (eq 2).[6]



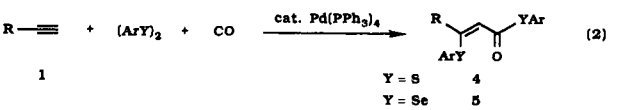


Table I. Addition of $(PhS)_2$ to 1-Octyne (**1a**) in the Presence of Several Transition-Metal Catalysts[a]

entry	catalyst	yield of **2a** (%)[b,c]	entry	catalyst	yield of **2a** (%)[b,c]
1	$Pd(PPh_3)_2Cl_2$	0	5	$Ni(PPh_3)_2Cl_2$	0
2	$Pd(PhCN)_2Cl_2$	0	6	$Pt(PPh_3)_4$	21
3	$Pd(OAc)_2$	0	7	$Rh(PPh_3)_3Cl$	24
4	$Pd(PPh_3)_4$	77	8	$Ru(PPh_3)_3Cl_2$	0

[a] All reactions were performed using 1.2 mmol of **1a**, 1.0 mmol of $(PhS)_2$, and 5 mol % of catalyst in Ph-H (2 mL) at 80 °C for 12 h. [b] Only *Z* isomer. [c] Determined by ^1H NMR.

Table II. Palladium(0)-Catalyzed Addition of $(PhS)_2$ to **1a**[a]

entry	$Pd(PPh_3)_4$ (mol %)	Ph-H (mL)	temp (°C)	time (h)	yield of **2a** (%)[b,c]
1	5	2	80	12	77
2	1	2	80	12	78
3	1	0.5	80	12	100 (91)
4	0.1	0.5	80	12	86
5	1	0.5	80	3	85
6	1	0.5	40	12	15

[a] Reaction of 1.0 mmol of **1a** and 1.0 mmol of $(PhS)_2$ in the presence of $Pd(PPh_3)_4$. [b] Only *Z* isomer. [c] NMR yield (isolated yield).

(1) For the disulfides, see: (a) Yamamoto, T.; Sekine, Y. *Inorg. Chim. Acta* **1984**, *83*, 47. (b) Gal, A. W.; Gosselink, J. W.; Vollenbroek, F. A. *Ibid.* **1979**, *32*, 235. (c) Canich, J. M.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R. *Inorg. Chem.* **1988**, *27*, 804. (d) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365. (e) Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2736. (f) Schermer, E. D.; Baddley, W. H. *J. Organomet. Chem.* **1971**, *27*, 83. (g) Pouly, S.; Tainturier, G.; Gautheron, B. *Ibid.* **1982**, *232*, C65 and references therein. For the diselenides, see: (h) Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, P679.

(2) For the transition-metal-catalyzed reaction using disulfides and diselenides, see: (a) Fukuzawa, S.; Fujinami, T.; Sakai, S. *Chem. Lett.* **1990**, 927. (b) Takahashi, H.; Ohe, K.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *334*, C43. (c) Kano, K.; Takeuchi, M.; Hashimoto, S.; Yoshida, Z. *Chem. Lett.* **1990**, 1381. (d) Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 2609.

(3) For the transition-metal-catalyzed reactions using organic sulfur and selenium compounds, see: (a) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1. (b) Luh, T. Y.; Ni, Z. J. *Synthesis* **1990**, 89. (c) Okamura, H.; Miura, M.; Kosugi, K.; Takei, H. *Tetrahedron Lett.* **1980**, *21*, 87. (d) Carpita, A.; Rossi, R.; Scamuzzi, B. *Ibid.* **1989**, *30*, 2699. (e) Cristau, H. J.; Chabaud, B.; Labaudiniere, R.; Christol, H. *J. Org. Chem.* **1986**, *51*, 875. (f) Murahashi, S.-I.; Yano, T. *J. Am. Chem. Soc.* **1980**, *102*, 2456. (g) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (h) Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4380. (i) McKervey, M. A.; Ratananukul, P. *Tetrahedron Lett.* **1982**, *23*, 2509. (j) Godleski, S. A.; Villhauer, E. B. *J. Org. Chem.* **1984**, *49*, 2246. (k) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1987**, *28*, 6321. (l) Dzhemilev, U. M.; Kunakova, R. V.; Gaisin, R. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *11*, 2655.

(4) For the synthetic utility of vinyl sulfides and selenides, see: (a) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075. (b) Magnus, P.; Quagliato, D. *J. Org. Chem.* **1985**, *50*, 1621. (c) Comasseto, J. V. *J. Organomet. Chem.* **1983**, *253*, 131 and references therein.

(5) During the course of our study, Dzhemilev et al. have reported the addition of $(PhS)_2$ to 1,3-diene catalyzed by a Ni complex to give the complicated mixture of adducts. See: Dzhemilev, U. M.; Kunakova, R. V.; Baibulatova, N. Z.; Mustafina, E. M.; Galkin, E. G.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, *3*, 747.

(6) For the synthetic utility of thiolesters, for example: (a) Masamune, S.; Hayase, Y.; Schilling, W.; Chan, W. K.; Bates, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 6756. (b) Anderson, R. J.; Henrick, C. A.; Rosenblum, L. D. *Ibid.* **1974**, *96*, 3654. For the synthetic utility of selenolesters, see: (c) Ogawa, A.; Sonoda, N. *Comprehensive Organic Synthesis Vol 6*; Winterfeldt, E., Ed.; Pergamon Press: Oxford, in press. (d) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4003. (e) Crich, D.; Fortt, S. M. *Tetrahedron Lett.* **1987**, *28*, 2895.

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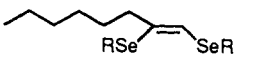
Table III. Palladium-Catalyzed Addition of $(RSe)_2$ to **1a**[a]



entry	$(RSe)_2$	yield (%)[b] (E/Z)[c]
1	$(PhSe)_2$	82 (0/100)
2	$(p\text{-}MeC_6H_4Se)_2$	76 (0/100)
3	$(p\text{-}CF_3C_6H_4Se)_2$	98 (0/100)
4	$(^nBuSe)_2$	24 (25/75)
5	$(PhCH_2Se)_2$	0

[a] Reactions were conducted under the conditions of 1.0 mmol of **1a** and 1.0 mmol of $(RSe)_2$ in the presence of 2 mol % of $Pd(PPh_3)_4$ for 12 h at 80 °C in Ph–H (0.5 mL). [b] Isolated yield. [c] Determined by ^1H NMR.

Results and Discussion

Reaction Conditions for the Addition of Disulfides and Diselenides to 1-Octyne (1a). We have found a new transition-metal-catalyzed reaction, i.e., the addition of diaryl disulfides to acetylenes to give *vic*-bis(arylthio)alkenes. The reaction of diphenyl disulfide (1.0 mmol) with 1-octyne (**1a**) (1.2 mmol) was examined in the presence of several transition-metal catalysts (5 mol %), and the results are summarized in Table I. The addition of $(PhS)_2$ to **1a** proceeded most effectively by use of $Pd(PPh_3)_4$ to stereoselectively give (*Z*)-1,2-bis(phenylthio)-1-octene (**2a**) in 77% yield (entry 4). $Pt(PPh_3)_4$ and $Rh(PPh_3)_3Cl$ also exhibited catalytic activity for this addition (entries 6 and 7). Other transition-metal complexes, such as Pd(II) complexes, $Ni(PPh_3)_2Cl_2$, and $Ru(PPh_3)_3Cl_2$, did not catalyze the reaction (entries 1, 2, 3, 5, and 8).

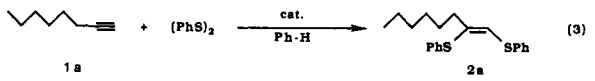
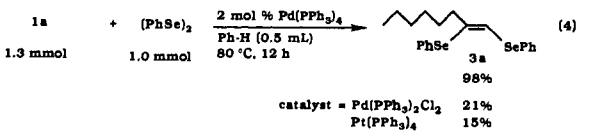


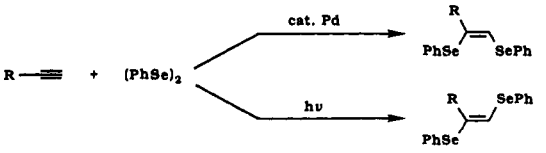
Table II indicates some results of the effects of varying the reaction conditions. Increasing the concentration of the substrate (>2 M) could reduce the amount of catalyst (entries 1, 2, and 4). Reaction at 40 °C proceeded very slowly and was not complete within 12 h (entry 6). The best results were obtained when the reaction was conducted at 80 °C for 12 h using 1 mol % of $Pd(PPh_3)_4$ and 0.5 mL of benzene (entry 3). Next, the addition of diphenyl diselenide to 1-octyne (**1a**) was examined under similar conditions as described in the case of the addition of diphenyl disulfide. Diphenyl diselenide also added to **1a** exclusively to give (*Z*)-1,2-bis(phenylseleno)-1-octene (**3a**) in an excellent yield (eq 4). Noteworthy is the fact that $Pd(PPh_3)_2Cl_2$ also exhibited



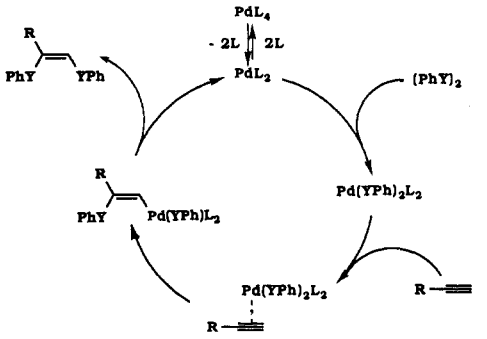
catalytic activity for the addition of $(PhSe)_2$, though the yield of adduct was not satisfactory. The addition also proceeded smoothly in THF (67 °C, 98%), CH_3CN (82 °C, 93%), and $CH_3C_6H_5$ (80 °C, 95%). Similar additions of some other diselenides to **1a** were also performed (Table III). Diaryl diselenides produced high yields of the corresponding 1,2-adducts (entries 1, 2, and 3), whereas the addition of dialkyl diselenides such as dibutyl diselenide resulted in a low yield of the desired 1,2-adduct (entry 4).[8] Dibenzyl diselenide did not add to **1a** (entry 5).

Addition of Diphenyl Disulfide and Diphenyl Diselenide to Various Acetylenes. The scope and limitations of the palladium-catalyzed addition of disulfides and diselenides to acetylenes are summarized in Table IV. In most cases, the reactions were clean and no byproduct was formed. Some functional groups, such as

Scheme I

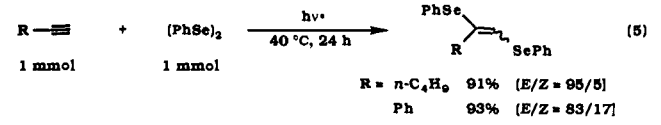


Scheme II. A Proposed Reaction Path for the Addition of $(PhY)_2$ (Y = S, Se) to Acetylene



hydroxy (entries 3–8), trimethylsilyl (entries 9, 10), and amino (entries 11, 12) groups, did not affect the addition of $(PhS)_2$ and $(PhSe)_2$. The addition proceeded stereoselectively to give the corresponding *Z* isomers almost exclusively.[9,10] The addition of bis(*p*-methylphenyl) diselenide to phenylacetylene was the only exception, giving a mixture of stereoisomers (E/Z = 15/85) (entry 14). Even in the thermal reaction without a palladium catalyst, phenylacetylene underwent the addition of $(p\text{-}MeC_6H_4Se)_2$ under similar conditions, and the E/Z ratio of the adducts was 83/17 (76% yield). Thus, the *E* isomer of the reaction in the presence of palladium catalyst would be generated by this competitive thermal addition.[11] In the case of the acetylenes bearing a carbon–carbon double bond, the addition took place chemoselectively to the triple bond, and no cyclization product was obtained (entries 17, 18). In contrast to terminal acetylenes as described above, the addition of disulfides and diselenides to the internal acetylenes like 4-octyne hardly proceeded (entry 16). On the other hand, the addition to propargyl bromide gave unidentified insoluble solids with recovery of $(PhSe)_2$ (entry 15).

As for the synthesis of 1,2-bis(phenylseleno)-1-alkenes, we have recently developed the methodology of the addition of diphenyl diselenide to acetylenes via a photoinitiated free radical mechanism.[12] As can be seen from the representative examples in eq 5, this radical reaction provided (*E*)-1,2-bis(phenylseleno)-1-alkenes, preferentially. Thus, the complementary methods, i.e.,



the palladium-catalyzed addition and the photoinitiated addition, present the routes to the stereoselective synthesis of (*Z*)- or (*E*)-1,2-bis(phenylseleno)-1-alkenes (Scheme I).

Stoichiometric Reaction. Graziani et al. have already reported that the stoichiometric reaction of diphenyl disulfide with Pd-

(7) (a) Abraham, W. D.; Cohen, T. *J. Am. Chem. Soc.* **1991**, *113*, 2313. (b) Nakagawa, I.; Hata, T. *Tetrahedron Lett.* **1975**, 1409. (c) Watanabe, Y.; Araki, T.; Ueno, Y.; Endo, T. *Ibid.* **1986**, *27*, 5385.

(8) The reaction of dibutyl disulfide with 1-octyne (**1a**) in the presence of $Pd(PPh_3)_4$ at 80 °C for 16 h gave the corresponding (*Z*)-1,2-adduct in only 9% yield (determined by ^1H NMR).

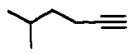
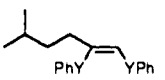
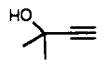
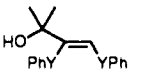
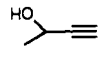
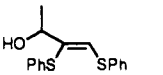
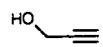
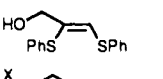
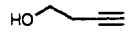
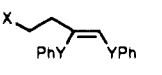
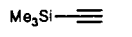
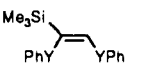
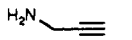
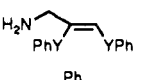
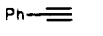
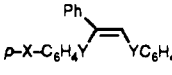
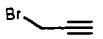
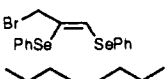
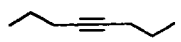
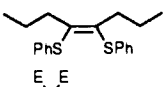
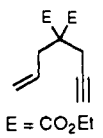
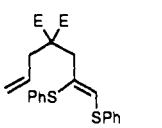
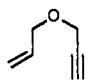
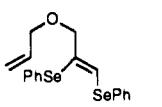
(9) The photoinitiated radical addition of disulfides to acetylenes has been reported to proceed in a less stereoselective manner. See: Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1967**, *32*, 3837.

(10) The stereochemistry and the ratios of the products were determined by NOE experiments and ^1H NMR spectroscopy, respectively.

(11) $(p\text{-}MeC_6H_4Se)_2$ was used to simplify the determination of the ratio E/Z by ^1H NMR spectroscopy. Considering the results of the reactions in the presence and absence of catalyst, the palladium catalyst would suppress the thermal addition.

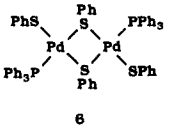
(12) For the photoinitiated addition of diselenides to acetylenes, see: (a) Ogawa, A.; Yokoyama, H.; Yokoyama, K.; Masawaki, T.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 5721. (b) Back, T. G.; Krishna, M. V. *Ibid.* **1988**, *53*, 2533.

Table IV. Palladium-Catalyzed Addition of $(ArY)_2$ (Y = S, Se) to Various Acetylenes[a]

entry	acetylene 1	$(ArY)_2$	product 2 or 3	yield of 2 or 3 (%)[b] (E/Z)[c]
1		$(PhS)_2$		Y = S, 98 (0/100)
2		$(PhSe)_2$		Y = Se, 79 (0/100)
3		$(PhS)_2$		Y = S, 89 (0/100)
4		$(PhSe)_2$		Y = Se, 96 (0/100)
5		$(PhS)_2$		87 (0/100)
6		$(PhS)_2$		79 (0/100)
7		$(PhS)_2$		Y = S, X = OH, 80 (0/100) X = SPh, 5[d] (0/100)
8		$(PhSe)_2$		Y = Se, X = OH, 84 (0/100)
9[e]		$(PhS)_2$		Y = S, 54 (1/99)
10[e]		$(PhSe)_2$		Y = Se, 66 (0/100)
11		$(PhS)_2$		Y = S, 66 (94)[f] (0/100)
12		$(PhSe)_2$		Y = Se, 90 (0/100)
13		$(PhS)_2$		X = H, Y = S, 85 (0/100)
14		$(p\text{-}MeC_6H_4Se)_2$		X = Me, Y = Se, 85 (15/85)[g]
15		$(PhSe)_2$		0
16[h]		$(PhS)_2$		5[c]
17		$(PhS)_2$		55 (0/100)
18		$(PhSe)_2$		58 (0/100)

[a] Reactions were conducted under the conditions of 1.0 mmol of acetylene 1 and 1.0 mmol of $(ArY)_2$ in the presence of $Pd(PPh_3)_4$ (1–2 mol %) for 12–20 h at 80 °C in Ph–H (0.5 mL). Reaction times were unoptimized. [b] Isolated yield. [c] Determined by ^1H NMR. [d] See ref 7. [e] The reaction was carried out without solvent at 70 °C in a sealed tube. [f] NMR yield. [g] See ref 11. [h] 5 mol % of $Pd(PPh_3)_4$, toluene reflux for 70 h.

$(PPh_3)_4$ gave the complex **6** formulated as a dimer having both terminal and bridged sulfide groups.[1c] The reaction of **6**[13] gen-



6

erated in situ with an equimolar amount of **1a** for 15 h at 65 °C afforded (*Z*)-1,2-bis(phenylthio)-1-octene (**2a**) in 65% yield (determined by ^1H NMR in C_6D_6). This fact does not contradict the hypothesis that the palladium-catalyzed addition of disulfide to acetylene proceeded via the oxidative addition of disulfide to Pd(0). A proposed reaction path includes the stereoselective insertion of acetylenes into the Pd–S bond to form *cis*-vinylpalladium and the subsequent reductive elimination of the product with retention of the stereochemistry (Scheme II).

The oxidative addition of diaryl ditellurides to $Pd(PPh_3)_4$ has been also reported to proceed readily,[14] but the corresponding palladium-catalyzed addition of diphenyl ditelluride to **1a** did not occur. At present, the reason why this reaction cannot apply to ditelluride is not clear.

Table V. The Effects of the Pressure of CO on the Carbonylative Addition of $(PhSe)_2$ to **1a**[a]

entry	CO (kg/cm²)	conversion (%)	yield[b] of **5a** (%) (E/Z)[c]	yield[b] of **3a** (%)[d]
1	5	100	77 (0/100)	16
2	15	100	87 (1/99)	7
3[e]	15	88	75 (0/100)	9
4	30	94	86 (0/100)	6
5	60	63	53 (1/99)	3
6[f]	4	78	78 (0/100)	0

[a] Reactions were carried out using 1.2 mmol of **1a**, 1.0 mmol of $(PhSe)_2$, 2 mol % of $Pd(PPh_3)_4$, and Ph–H (0.5 mL) at 80 °C for 15 h. [b] Isolated yield. [c] Determined by ^1H NMR. [d] Only *Z* isomer. [e] Toluene (0.5 mL) was used as a solvent. [f] Cat. $Pd(PPh_3)_2Cl_2$, 30 h.

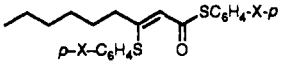
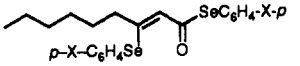
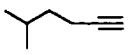
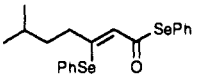
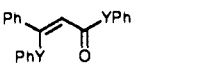
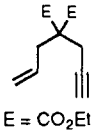
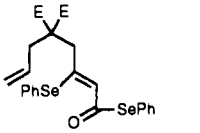
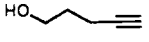
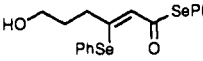
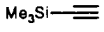
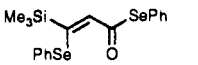
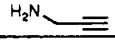
Reaction Conditions for the Carbonylative Addition of Diphenyl Diselenide to 1-Octyne (1a). It is of much interest that the present reaction is carried out in the presence of carbon monoxide, because there is a possibility that the carbonylative addition of dichalcogenides and CO to acetylenes will occur. Thus, the reaction of 1-octyne (**1a**) (1.0 mmol) with diphenyl diselenide (1.0 mmol) was attempted in the presence of 2 mol % of $Pd(PPh_3)_4$ under an atmosphere of carbon monoxide in toluene (2 mL) at 80 °C for 19 h. As we envisioned, the reaction gave the carbonylated product (*Z*)-1,3-(phenylseleno)-2-nonen-1-one (**5a**)[15] (29%) together with

(13) The structure of this complex in solution is still undetermined. The palladium complexes having benzenethiolate ligands often form the polymeric complexes. See: (a) Rauchfuss, T. B.; Shu, J. S.; Roundhill, D. M. *Inorg. Chem.* **1976**, *15*, 2096. (b) Schott, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 877. (c) Woodward, P.; Dahl, L. F.; Abel, E. W.; Crosse, B. C. *J. Am. Chem. Soc.* **1965**, *87*, 5251.

(14) Chia, L. Y.; McWhinnie, W. R. *J. Organomet. Chem.* **1978**, *148*, 165.

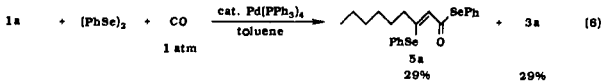
(15) The stereochemistry of compound **5a** was confirmed by NOESY experiment, and the regiochemistry was determined from the result of the reduction of **5a** with tributyltin hydride. For the reduction of selenolesters with tin hydride, see: Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328.

Table VI. Palladium-Catalyzed Carbonylative Addition of Diaryl Disulfides and Diaryl Diselenides to Acetylenes in the Presence of CO[a]

entry	acetylene	$(ArY)_2$	catalyst	CO (kg/cm^2)	time (h)	product **4** or **5**	yield (%) **4** or **5** (*E*/*Z*)	yield (%) **2** or **3**
1		$(PhS)_2$	$Pd(PPh_3)_4$	15	15		X = H, 56 (0/100)	27
2				60	39		X = H, 84 (0/100)	5
3			$Pd(PPh_3)_2Cl_2$	15	26		X = H, 75 (6/94)	0
4		$(p\text{-}MeC_6H_4S)_2$	$Pd(PPh_3)_4$	60	26		X = Me, 86 (0/100)	7
5		$(p\text{-}MeC_6H_4Se)_2$		15	18		X = Me, 80 (0/100)	7
6		$(p\text{-}CF_3C_6H_4Se)_2$		15	18		X = CF_3, 89 (2/98)	8
7		$(PhSe)_2$		15	15		76 (0/100)	6
8		$(PhSe)_2$	$Pd(PPh_3)_2Cl_2$[b]	15	30		Y = Se, 86 (3/97)	12
9		$(PhS)_2$	$Pd(PPh_3)_2Cl_2$[b]	15	44		Y = S, 29 (3/97)	0
10[c]		$(PhSe)_2$	$Pd(PPh_3)_2Cl_2$	10	16		60 (0/100)	0
11		$(PhSe)_2$	$Pd(PPh_3)_4$	15	15		76 (8/92)	6
12		$(PhSe)_2$	$Pd(PPh_3)_2Cl_2$[b]	15	37		trace	0
13		$(PhSe)_2$	$Pd(PPh_3)_4$	30	19		a complicated mixture	

[a] Reactions were conducted under the conditions of 1.0 mmol of acetylene, 1.0 mmol of $(ArY)_2$, and CO in the presence of 2.0 mol % of catalyst at 80 °C in a 50-mL stainless autoclave in Ph–H (0.5–1.0 mL). [b] 5 mol %. [c] 110 °C.

the direct adduct of diselenide, **3a** (29%) (eq 6). Table V summarizes the results of the carbonylative addition of diphenyl diselenide to **1a** with the aid of palladium catalysts under various pressures of carbon monoxide.



The reaction under pressurized carbon monoxide substantially suppressed the generation of **3a** and improved the yield of **5a** (entries 1, 2). Under the pressure at 60 kg/cm^2, however, the reaction was retarded and was not complete in 15 h (entry 5). Among the other transition-metal catalysts examined [$Pd(dppe)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PhCN)_2Cl_2$, $Pd(OAc)_2$, $Ni(PPh_3)_2Cl_2$, $Rh(PPh_3)_3Cl$, $Co_2(CO)_8$,[16] $Cr(CO)_6$], $Pd(PPh_3)_2Cl_2$ and $Pd(PhCN)_2Cl_2$ also catalyzed the carbonylation. It should be noted that, in the case of $Pd(PPh_3)_2Cl_2$, the carbonylative addition proceeded smoothly and the formation of the direct adduct **3a** was suppressed despite the reaction being run under a relatively lower pressure of CO (4 kg/cm^2) (entry 6 vs eq 4).[17]

Carbonylative Addition of Diaryl Disulfide and Diaryl Diselenide to Various Acetylenes. The procedure for the carbonylative addition with carbon monoxide was also applicable to the diphenyl disulfide/acetylene reaction system. The reaction of $(PhS)_2$ with 1 equiv of **1a** in the presence of 2 mol % of $Pd(PPh_3)_4$ under pressure of CO (15 kg/cm^2) provided the desired carbonylative addition product **4a** in 56% yield with 27% of the direct adduct of disulfide **2a**. Again, the excellent stereo- and regioselectivity of the introduction of carbon monoxide were achieved in this reaction. Higher pressure (60 kg/cm^2), compared with the case of diselenides, was essential for the suppression of the generation of **2a** when $Pd(PPh_3)_4$ was used as a catalyst (entries 1, 2 in Table VI vs entry 2 in Table V). $Pd(PPh_3)_2Cl_2$ catalyzed the carbonylative addition even under a low pressure of CO, while the reaction was accompanied by the formation of a slight yield of *E* isomer.

Scheme III. A Proposed Reaction Path for the Carbonylative Addition of $(PhY)_2$ (Y = S, Se) to Acetylene

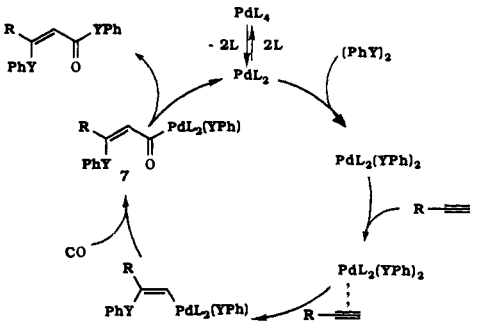


Table VI summarizes the results of the carbonylative addition of disulfides and diselenides to various acetylenes. This carbonylation was completely regioselective and highly stereoselective; the carbonyl group was introduced only at the terminal carbon of acetylenes, and *Z* isomers were obtained. The $Pd(PPh_3)_4$-catalyzed reaction of phenylacetylene gave the direct adducts as the major product (not shown). When $Pd(PPh_3)_2Cl_2$ was used, however, the carbonylation proceeded with a preference for the direct 1,2-addition (entries 8, 9). Acetylenes bearing a carbon–carbon double bond reacted chemoselectively at the triple bond (entry 10).[18] The hydroxy group did not interfere with the carbonylative addition (entry 11).[19] In contrast, propargylamine afforded a complicated mixture of undetermined products, though the 1,2-addition of $(PhSe)_2$ to this substrate took place efficiently in the absence of CO (entry 13 in Table VI vs entry 12 in Table IV). The carbonylation of (trimethylsilyl)acetylene scarcely proceeded (entry 12 in Table VI vs entry 10 in Table IV).

When the reaction of (*Z*)-1,2-bis(phenylseleno)-1-octene (**3a**) with carbon monoxide was conducted in the presence of $Pd(PPh_3)_4$ under similar conditions, no CO-incorporated products were

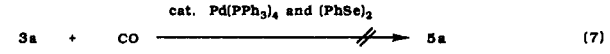
(16) It has been reported that the reaction of diaryl diselenides and disulfides with carbon monoxide in the presence of $Co_2(CO)_8$ gave the selenolesters and thiolesters; see ref 2b,d.

(17) This extent of pressure was necessarily to avoid the generation of byproducts.

(18) In the case of the carbonylative addition of $(PhS)_2$ to this substrate, the cyclization reaction also occurred. The details are now under investigation.

(19) Acetylenes having a hydroxy group at the position α or β to the carbon–carbon triple bond provided lactones. The details will be published in the near future.

formed (eq 7). This result indicates that **3** is not a precursor for



(7)

the carbonylation. Two different reaction paths can be proposed on the basis of the regio- and stereochemistry of this carbonylative addition. One involves the formation of vinylpalladium **7**, in which palladium bonds to the terminal position followed by the insertion of carbon monoxide (Scheme III). The other possibility is the initial formation of an ArYCO[Pd]YAr **8** (Y = S or Se)[16,20] species, subsequent addition to an acetylene, and reductive elimination of the product. Yet it is not specified whether the carbonylation occurs via these pathways or occurs via a more complex sequence, and we are now occupied with this problem.

Conclusions

$Pd(PPh_3)_4$ did effectively catalyze the addition of diaryl disulfides to various terminal acetylenes to give high yields of *Z* adducts. While $Pt(PPh_3)_4$ and $Rh(PPh_3)_3Cl$ catalysts could be employed with varying degrees of success, $Pd(PPh_3)_4$ appeared to be superior. Diaryl diselenides also successfully added to acetylenes. However, dibutyl diselenide gave a poor yield of product, and dibenzyl diselenide did not add at all. An internal acetylene such as 4-octyne hardly undergoes the addition in this palladium-catalyzed addition. When this reaction was carried out in the presence of carbon monoxide, carbonylative addition occurred to give the (*Z*)-1,3-bis(arylthio)-2-alken-1-ones **4** and (*Z*)-1,3-bis(arylseleno)-2-alken-1-ones **5**, respectively. The carbonylation was completely regioselective and highly stereoselective. $Pd(PPh_3)_2Cl_2$ also effectively catalyzed the carbonylative addition. These reactions were not applicable to diphenyl ditelluride, though the oxidative addition of $(ArTe)_2$ to $Pd(PPh_3)_4$ easily occurs. We believe that this study will open up a new field of transition-metal chemistry in combination with sulfur and selenium chemistry.

Experimental Section

Unless otherwise noted, acetylenes and catalysts were obtained commercially and the former were purified for use by distillation. Diphenyl disulfide and bis(*p*-methylphenyl) disulfide were purified by recrystallization from EtOH or *n*-hexane and dried in vacuo. Diphenyl diselenide was prepared according to the literature[21] and was recrystallized from *n*-hexane. The same procedure was employed for the syntheses of bis(*p*-methylphenyl) diselenide and bis[*p*-(trifluoromethyl)phenyl] diselenide. Dibenzyl diselenide and dibutyl diselenide were prepared according to the procedures which we have recently developed[22] and were purified by distillation or flash chromatography on silica gel (*n*-hexane). Enynes were prepared according to the literature methods.[23] Benzene and toluene were purified by distillation from a sodium–lead (>8%) alloy before use.

^1H NMR spectra of $CDCl_3$ solutions were recorded with a JEOL JNM-GSX-270 (270 MHz) spectrometer. Me_4Si served as the internal standard. ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a JEOL JNM-GSX-270 (68 MHz) spectrometer. Chemical shifts in the ^{13}C NMR spectra were determined relative to Me_4Si. IR spectra were recorded on a Perkin-Elmer Model 1600 spectrometer. Mass spectra were recorded with a JEOL JMS-DX303. High-resolution mass spectra (HRMS) and combustion analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University.

Palladium-Catalyzed Addition: General Procedure (Tables II, III, and IV). (*Z*)-1,2-Bis(phenylthio)-1-octene (2a) (Table II, Entry 3). Into a two-necked flask equipped with a reflux condenser and a magnetic stirring bar were placed tetrakis(triphenylphosphine)palladium (24 mg, 0.02 mmol), diphenyl disulfide (218 mg, 1.0 mmol), 1-octyne (110 mg, 1.0 mmol), and benzene (0.5 mL) under an argon atmosphere. The color of the solution rapidly turned from yellow to dark brown. The mixture was refluxed with stirring for 12 h. After the reaction was complete, the resulting catalyst was removed by filtration through Celite, and the filtrate was evaporated under reduced pressure. The residual mixture was purified by medium-pressure liquid chromatography (MPLC) and preparative TLC (PTLC) to give 300 mg (91%) of (*Z*)-1,2-bis(phenylthio)-1-octene as a clear oil. MPLC of the reaction mixtures were performed with Merck 25–40 μm mesh silica gel (Art 9390). PTLC was carried out using Wakogel B-5F silica gel.

2a: ^1H NMR (270 MHz, $CDCl_3$) δ 0.84 (t, 3 H, *J* = 6.6 Hz), 1.20 (m, 6 H), 1.49 (m, 2 H), 2.24 (t, 2 H, *J* = 7.5 Hz), 6.56 (s, 1 H), 7.12–7.43 (m, 10 H) (NOE experiment: Irradiation of the C-3 methylene triplet at δ 2.24 resulted in a 7% enhancement of the signal at δ 6.56 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.05, 22.53, 28.47, 31.51, 37.10, 126.73, 126.82, 128.94, 129.04, 129.08, 129.69, 130.48, 133.81, 134.40, 135.87; IR (NaCl) 3071, 3057, 2953, 2926, 1582, 1477, 739, 690 cm^{-1}; mass spectrum (EI), *m/e* 328 (M^+, 100). Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36; S, 19.52. Found: C, 73.28; H, 7.42; S, 19.44.

The solvent (hexane/Et_2O) was used as eluent in the following ratios: 10:0 (entries 1–4 in Table III and entries 1–2, 9–10, 13–14 in Table IV), 1.5:1 (entries 3–8), 4:1 (entries 17–18), 2:1 containing Et_3N (entries 11, 12). Reactions were carried out for 12–20 h. Reaction time was unoptimized. Dichalcogen compounds and yields are listed in Tables III and IV. The following compounds were prepared according to the general procedure.

(*Z*)-1,2-Bis(phenylseleno)-1-octene (3a) (Table III, entry 1): oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, 3 H, *J* = 6.7 Hz), 1.24 (m, 6 H), 1.47 (m, 2 H), 2.29 (t, 2 H, *J* = 8.1 Hz), 6.95 (s, 1 H), 7.12–7.64 (m, 10 H) (NOE experiment: Irradiation of the C-3 methylene triplet at δ 2.29 resulted in a 10% enhancement of the signal at δ 6.95 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.95, 22.40, 28.27, 28.75, 31.37, 39.78, 127.12, 127.18, 127.73, 129.01, 129.10, 129.36, 131.10, 132.43, 132.74, 136.24; IR (NaCl) 3068, 2925, 1577, 1475, 1437, 1024, 734, 690 cm^{-1}; mass spectrum (EI), *m/e* 424 (M^+, 100). Anal. Calcd for $C_{20}H_{24}Se_2$: C, 56.88; H, 5.73. Found: C, 57.03; H, 5.78.

(*Z*)-1,2-Bis[(*p*-methylphenyl)seleno]-1-octene (Table III, entry 2): oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.84 (t, 3 H, *J* = 6.8 Hz), 1.15–1.27 (m, 6 H), 1.45 (quintet, 2 H, *J* = 7.6 Hz), 2.23 (t, 2 H, *J* = 7.6 Hz), 2.32 (s, 6 H), 6.83 (s, 1 H), 7.06–7.11 (m, 4 H), 7.40–7.47 (m, 4 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.23 resulted in a 18% enhancement of the signal at δ 6.83 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.06, 21.10, 22.53, 28.40, 28.84, 31.51, 39.65, 125.67, 127.18, 127.54, 129.94, 130.02, 132.89 (J_{Se-C} = 11.0 Hz), 133.42 (J_{Se-C} = 11.0 Hz), 136.37, 137.32; IR (NaCl) 3017, 2954, 2925, 2855, 1489, 1456, 1016, 802 cm^{-1}; mass spectrum (EI), *m/e* 452 (M^+, 100). Anal. Calcd for $C_{22}H_{28}Se_2$: C, 58.67; H, 6.62. Found: C, 58.49; H, 6.61.

(*Z*)-1,2-Bis[[(*p*-trifluoromethyl)phenyl]seleno]-1-octene (Table III, entry 3): oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, 3 H, *J* = 6.3 Hz), 1.18–1.33 (m, 6 H), 1.52 (m, 2 H), 2.36 (t, 2 H, *J* = 7.5 Hz), 7.07 (s, 1 H, J_{Se-H} = 18.9 Hz), 7.52 (d, 2 H, *J* = 8.8 Hz), 7.55 (d, 2 H, *J* = 8.8 Hz), 7.58 (d, 2 H, *J* = 8.8 Hz), 7.64 (d, 2 H, *J* = 8.8 Hz) (NOE experiment: Irradiation of the C-3 methylene triplet at δ 2.36 resulted in a 15% enhancement of the signal at δ 7.07 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.04, 22.60, 28.50, 28.99, 31.56, 40.57, 124.10 (q, *J* = 272.2 Hz), 124.16 (q, *J* = 271.6 Hz), 126.04 (q, *J* = 3.7 Hz), 126.10 (q, *J* = 3.7 Hz), 129.23, 129.36 (q, *J* = 32.6 Hz), 129.65 (q, *J* = 32.8 Hz), 131.84 (J_{Se-C} = 11.6 Hz), 132.18 (J_{Se-C} = 11.6 Hz), 134.87, 136.14, 136.78; IR (NaCl) 2929, 1602, 1398, 1326, 1165, 1127, 1077, 827 cm^{-1}; mass spectrum (EI), *m/e* 560 (M^+, 100); exact mass (M^+) calcd for $C_{22}H_{22}F_6Se_2$ 559.9955, found 559.9937.

1,2-Bis(*n*-butylseleno)-1-octene (Table III, Entry 4). *Z* isomer: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.86–0.95 (m, 9 H), 1.24–1.34 (m, 6 H), 1.38–1.57 (m, 6 H), 1.66 (quintet, 2 H, *J* = 7.8 Hz), 1.70 (quintet, 2 H, *J* = 7.8 Hz), 2.30 (t, 2 H, *J* = 7.3 Hz), 2.70 (t, 2 H, *J* = 7.8 Hz), 2.73 (t, 2 H, *J* = 7.8 Hz), 6.55 (s, 1 H, J_{Se-H} = 14 Hz) (NOE experiment: Irradiation of the C-3 methylene triplet at δ 2.30 resulted in a 17% enhancement of the signal at δ 6.55 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.61, 13.62, 14.10, 22.64, 22.86, 23.03, 25.24, 26.51, 28.71, 28.97, 31.68, 32.69, 33.08, 39.98, 124.44 133.79; IR (NaCl) 2956, 2927, 2856, 1574, 1464, 1478, 1257, 1196, 735 cm^{-1}; mass spectrum (EI), *m/e* 384 (M^+, 100); exact mass (M^+) calcd for $C_{16}H_{32}Se_2$ 384.0834, found 384.0846. *E* isomer: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.85–0.94 (m, 9 H), 1.30–1.55 (m, 12 H), 1.66 (quintet, 2 H, *J* = 7.8 Hz), 1.68 (quintet, 2 H, *J* = 7.8 Hz), 2.35 (t, 2 H, *J* = 7.3 Hz), 2.70 (t, 2 H, *J* = 7.8 Hz), 2.73 (t, 2 H, *J* = 7.8 Hz), 6.37 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.58, 13.61, 14.10, 22.61, 22.80, 23.03, 26.02, 27.02, 28.38, 28.82, 31.62, 32.11, 32.97, 37.01, 118.80, 131.95; IR (NaCl) 2957, 2927, 2856, 1574, 1464, 1258, 1199, 1118 cm^{-1}; mass spectrum (EI), *m/e* 384 (M^+, 100). Anal. Calcd for $C_{16}H_{32}Se_2$: C, 50.26; H, 8.44. Found: C, 50.64; H, 8.50.

(20) Kim, Y. J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182.
(21) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(22) (a) Nishiyama, Y.; Katsuura, A.; Negoro, A.; Hamanaka, S.; Miyoshi, N.; Yamana, Y.; Ogawa, A.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 3776. (b) Sekiguchi, M.; Tanaka, H.; Takami, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *Heteroat. Chem.* **1991**, *2*, 427.
(23) (a) Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 4967. (b) Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, *25*, 4041.

(*Z*)-1,2-Bis(phenylthio)-5-methyl-1-hexene (Table IV, entry 1): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.80 (d, 6 H, J = 6.4 Hz), 1.36–1.49 (m, 3 H), 2.25 (t, 2 H, J = 7.3 Hz), 6.56 (s, 1 H), 7.20–7.43 (m, 10 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.25 resulted in a 16% enhancement of the signal at δ 6.56 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.37, 27.35, 30.91, 35.04, 37.83, 126.79, 128.64, 128.93, 129.08, 129.68, 130.63, 133.73, 134.80, 135.88; IR (NaCl) 3058, 2954, 2854, 2867, 1582, 1478, 1438, 740, 690 cm^{-1}; mass spectrum (EI), m/e 314 (M^+, 73). Anal. Calcd for $C_{19}H_{22}S_2$: C, 72.56; H, 7.05; S, 20.39. Found: C, 72.26; H, 6.92; S, 20.14.

(*Z*)-1,2-Bis(phenylseleno)-5-methyl-1-hexene (Table IV, entry 2): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.78 (d, 6 H, J = 6.1 Hz), 1.34–1.48 (m, 3 H), 2.28 (t, 2 H, J = 7.5 Hz), 6.93 (s, 1 H), 7.26–7.30 (m, 6 H), 7.52–7.57 (m, 4 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.28 resulted in a 6% enhancement of the signal at δ 6.93 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.38, 27.33, 37.88, 38.23, 127.29, 127.35, 129.16, 129.26, 129.49, 131.28, 132.60, 133.11, 136.89; IR (NaCl) 3070, 3056, 2954, 1578, 1476, 1438, 1022, 736, 690 cm^{-1}; mass spectrum (EI), m/e 410 (M^+, 18). Anal. Calcd for $C_{19}H_{22}Se_2$: C, 55.89; H, 5.43. Found: C, 55.76; H, 5.53.

(*Z*)-1,2-Bis(phenylthio)-3-hydroxy-3-methyl-1-butene (Table IV, entry 3): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.44 (s, 6 H), 2.30 (br s, 1 H), 7.11–7.41 (m, 11 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.29, 75.07, 125.63, 126.95, 127.47, 128.98, 129.16, 130.60, 134.86, 134.91, 137.84; IR (NaCl) 3399, 2976, 1581, 1478, 1439, 738, 690 cm^{-1}; mass spectrum (EI), m/e 302 (M^+, 6). Anal. Calcd for $C_{17}H_{18}OS_2$: C, 67.51; H, 5.60; S, 21.20. Found: C, 67.26; H, 5.98; S, 21.32.

(*Z*)-1,2-Bis(phenylseleno)-3-hydroxy-3-methyl-1-butene (Table IV, entry 4): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.45 (s, 6 H), 2.14 (br s, 1 H), 7.14–7.31 (m, 6 H), 7.47–7.56 (m, 4 H), 7.61 (s, 1 H, J_{Se-H} = 10.7 Hz) (NOE experiment (benzene-d_6): Irradiation of the methyl singlet at δ 1.63 (which corresponds to the singlet at δ 1.45 in $CDCl_3$) resulted in an 8% enhancement of the signal at δ 8.09 (δ 7.61 in $CDCl_3$) (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.37, 75.82, 126.52, 127.77, 129.26, 129.29, 129.88 (J_{Se-C} = 12.0 Hz), 130.33, 130.67, 133.24 (J_{Se-C} = 10.0 Hz), 136.79, 139.01; IR (NaCl) 3428, 3056, 2974, 1577, 1476, 1438, 736, 690 cm^{-1}; mass spectrum (CI), m/e 381 ($M^+ + 1 - H_2O$, 100). Anal. Calcd for $C_{17}H_{18}OSe_2$: C, 51.52; H, 4.57. Found: C, 51.33; H, 4.81.

(*Z*)-1,2-Bis(phenylthio)-3-hydroxy-1-butene (Table IV, entry 5): oil; ^{1}H NMR 270 MHz, $CDCl_3$) δ 1.36 (d, 3 H, J = 6.1 Hz), 2.28 (d, 1 H, J = 4.3 Hz), 4.36 (quintet, 1 H, J = 4.3, 6.1 Hz), 7.15–7.49 (m, 11 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.76, 71.07, 126.39, 127.50, 128.62, 129.14, 129.21, 130.57, 133.15, 134.10, 134.85, 136.12; IR (NaCl) 3372, 3057, 2974, 1581, 1478, 1439, 1024, 741, 690 cm^{-1}; mass spectrum (EI), m/e 288 (M^+, 4). Anal. Calcd for $C_{16}H_{16}OS_2$: C, 66.63; H, 5.59. Found: C, 66.64; H, 5.65.

(*Z*)-1,2-Bis(phenylthio)-3-hydroxy-1-propene (Table IV, entry 6): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.89 (t, 1 H, J = 6.0 Hz), 4.16 (d, 2 H, J = 6.0 Hz), 7.03 (s, 1 H), 7.20–7.47 (m, 10 H) (NOE experiment: Irradiation of the methylene doublet at δ 4.16 resulted in an 18% enhancement at δ 7.03 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 65.45, 126.97, 127.47, 129.19, 129.22, 129.77, 129.83, 130.48, 133.07, 134.74, 134.87; IR (NaCl) 3369, 3058, 2914, 1580, 1478, 1438, 740, 689 cm^{-1}; mass spectrum (EI), m/e 274 (M^+, 100). Anal. Calcd for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14. Found: C, 65.54; H, 5.23.

(*Z*)-1,2-Bis(phenylthio)-4-hydroxy-1-butene (Table IV, entry 7): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.68 (br s, 1 H), 2.49 (t, 2 H, J = 6.2 Hz), 3.71 (t, 2 H, J = 6.2 Hz), 6.72 (s, 1 H), 7.21–7.46 (m, 10 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.49 resulted in 18% enhancement at δ 6.72 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 40.08, 60.84, 127.02, 127.17, 129.10, 129.16, 129.19, 130.05, 130.38, 132.95, 133.38, 135.26; IR (NaCl) 3354, 3056, 2932, 1582, 1478, 1439, 1024, 741 cm^{-1}; mass spectrum (EI), m/e 288 (M^+, 34). Anal. Calcd for $C_{16}H_{16}OS_2$: C, 66.63; H, 5.59; S, 22.23. Found: C, 66.58; H, 5.64; S, 22.05.

(*Z*)-1,2,4-Tris(phenylthio)-1-butene (Table IV, entry 7): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.56 (t, 2 H, J = 7.3 Hz), 3.07 (t, 2 H, J = 7.3 Hz), 6.65 (s, 1 H), 7.11–7.44 (m, 15 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.56 resulted in 22% enhancement at δ 6.65 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 31.46, 35.78, 124.90, 125.98, 126.12, 127.88, 128.05, 128.12, 128.15, 129.04, 129.36, 129.73, 131.51, 132.32, 134.33, 134.91; IR (NaCl) 3057, 2922, 1582, 1479, 1438, 739, 690 cm^{-1}; mass spectrum (EI), m/e 380 (M^+, 9). Anal. Calcd for $C_{22}H_{20}S_3$: C, 69.43; H, 5.29; S, 25.27. Found: C, 69.11; H, 5.29; S, 24.91.

(*Z*)-1,2-Bis(phenylseleno)-4-hydroxy-1-butene (Table IV, entry 8): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.77 (t, 1 H, J = 5.8 Hz), 2.52 (t, 2 H, J = 5.6 Hz), 3.69 (q, 2 H, J = 5.6, 5.8 Hz), 7.09 (s, 1 H, J_{Se-H} = 16.9 Hz), 7.26–7.34 (m, 6 H), 7.51–7.59 (m, 4 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.52 resulted in 5% enhancement at δ 7.09 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 42.83, 61.08, 127.56, 127.61, 129.14, 129.34, 129.37, 130.77, 131.18, 131.81 (J_{Se-C} = 17 Hz), 132.85 (J_{Se-C} = 10 Hz); IR (NaCl) 3354, 3055, 2933, 1577, 1476, 1438, 1066, 1046, 1022, 737, 691 cm^{-1}; mass spectrum (EI), m/e 384 (M^+, 26). Anal. Calcd for $C_{16}H_{16}OSe_2$: C, 50.28; H, 4.22. Found: C, 49.97; H, 4.49.

(*Z*)-1,2-Bis(phenylthio)-1-(trimethylsilyl)ethene (Table IV, entry 9): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 7.12–7.51 (m, 11 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ −1.17, 125.68, 127.48, 128.34, 128.66, 129.16, 130.00, 130.72, 135.18, 135.80, 148.66; IR (NaCl) 3058, 2954, 1582, 1510, 1478, 1439, 1248, 929, 837, 739 cm^{-1}; mass spectrum (EI), m/e 316 (M^+, 100). Anal. Calcd for $C_{17}H_{20}S_2Si$: C, 64.50; H, 6.37; S, 20.26. Found: C, 64.50; H, 6.42; S, 19.97.

(*Z*)-1,2-Bis(phenylseleno)-1-(trimethylsilyl)ethene (Table IV, entry 10): oil; ^{1}H NMR (270 MHz, $CDCl_3$, 1,4-dioxane (δ 3.69) as the internal standard) δ 0.05 (s, 9 H), 7.19–7.24 (m, 3 H), 7.31–7.33 (m, 3 H), 7.45–7.47 (m, 2 H), 7.58–7.60 (m, 2 H), 7.87 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$, $CDCl_3$ (δ 77.02) as the internal standard) δ −1.13, 126.48, 127.76, 128.99, 129.33, 130.89, 130.99, 131.08, 133.40 (J_{Se-C} = 12.0 Hz), 149.27 (J_{Se-C} = 12.0 Hz); IR (NaCl) 2954, 1578, 1520, 1476, 1438, 1247, 888, 840, 753, 690 cm^{-1}; mass spectrum (EI), m/e 412 (M^+, 3). Anal. Calcd for $C_{17}H_{20}Se_2Si$: C, 49.76; H, 4.91. Found: C, 49.48; H, 5.01.

(*Z*)-1,2-Bis(phenylthio)-3-amino-1-propene (Table IV, entry 11): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.40 (s, 2 H), 3.38 (s, 2 H), 6.86 (s, 1 H), 7.23–7.46 (m, 10 H) (NOE experiment: Irradiation of the methylene singlet at δ 3.38 resulted in a 7% enhancement of the signal at δ 6.86 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 47.71, 126.87, 127.30, 129.16, 129.18, 129.96, 130.31, 132.08, 133.27, 133.73, 135.10; IR (NaCl) 3375, 3056, 2912, 1654, 1581, 1477, 1438, 1024, 816, 744, 690 cm^{-1}; mass spectrum (EI), m/e 273 (M^+, 100). Anal. Calcd for $C_{15}H_{15}NS_2$: C, 65.89; H, 5.53; N, 5.12. Found: C, 65.53; H, 5.71; N, 4.73.

(*Z*)-1,2-Bis(phenylseleno)-3-amino-1-propene (Table IV, entry 12): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.43 (br s, 2 H), 3.38 (br s, 2 H), 7.22 (s, 1 H), 7.26–7.33 (m, 6 H), 7.51–7.61 (m, 4 H) (NOE experiment (in benzene-d_6): Irradiation of the methylene singlet at δ 3.18 (which corresponds to the singlet at δ 3.38 in $CDCl_3$) resulted in a 14% enhancement of the signal at δ 7.12 (δ 7.22 in $CDCl_3$) (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 50.24, 127.46, 127.73, 128.88, 129.36, 129.39, 130.60, 130.81, 132.51 (J_{Se-C} = 12.0 Hz), 133.12 (J_{Se-C} = 12.0 Hz); IR (NaCl) 3369, 3054, 2360, 1577, 1476, 1437, 1021, 841, 736 cm^{-1}; mass spectrum (EI), m/e 369 (M^+, 9). Anal. Calcd for $C_{15}H_{15}NSe_2$: C, 49.06; H, 4.12; N, 3.81. Found: C, 49.43; H, 4.43; N, 3.93.

(*Z*)-1,2-Bis(phenylthio)styrene (Table IV, entry 13): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.06–7.56 (m, 16 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 125.82, 126.68, 127.50, 127.55, 128.13, 128.35, 128.81, 129.24, 129.31, 130.40, 134.64, 135.13, 136.50, 138.66; IR (NaCl) 3054, 1580, 754, 739, 689 cm^{-1}; mass spectrum (EI), m/e 320 (M^+, 100). Anal. Calcd for $C_{20}H_{16}S_2$: C, 74.96; H, 5.03. Found: C, 75.12; H, 5.26.

(*Z*)-1,2-Bis[(*p*-methylphenyl)seleno]styrene (Table IV, Entry 14). Containing 15% of the *E* isomer: oil; ^{1}H NMR (270 MHz, $CDCl_3$) (*Z* isomer) δ 2.23 (s, 3 H,), 2.34 (s, 3 H), 6.95–7.52 (m, 14 H), (*E* isomer) δ 2.27 (s, 3 H), 2.30 (s, 3 H), 6.95–7.52 (m, 14 H); ^{13}C NMR (68 MHz, $CDCl_3$) (*Z* isomer) δ 21.02, 21.14, 126.54, 127.28, 127.33, 128.20, 129.91, 130.16, 131.18, 131.39, 132.32, 133.48, 136.20, 136.54, 137.91, 140.66; IR (NaCl) 3013, 2966, 2916, 1591, 1487, 1440, 1264, 1014, 801 cm^{-1}; mass spectrum (EI), m/e 444 (M^+, 95). Anal. Calcd for $C_{22}H_{20}Se_2$: C, 59.74; H, 4.56. Found: C, 59.99; H, 4.71.

(*Z*)-1,2-Bis(phenylthio)-4,4-dicarbethoxyhepta-1,6-diene (Table IV, entry 17): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.16 (t, 6 H, J = 7.2 Hz), 2.78 (d, 2 H, J = 7.2 Hz), 2.98 (s, 2 H), 4.01–4.02 (m, 4 H), 5.02–5.09 (m, 2 H), 5.55–5.56 (m, 1 H), 6.87 (s, 1 H), 7.19–7.43 (m, 10 H) (NOE experiment: Irradiation of the methylene singlet at δ 2.98 resulted in a 19% enhancement of the signal at δ 6.87 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.91, 36.62, 38.63, 57.60, 61.39, 119.18, 124.48, 126.24, 127.38, 128.42, 129.09, 129.19, 130.32, 132.47, 134.13, 134.97, 140.10, 170.48; IR (NaCl) 3075, 2981, 1732, 1583, 1479, 1440, 742, 692 cm^{-1}; mass spectrum (EI), m/e 456 (M^+, 99). Anal. Calcd for $C_{25}H_{28}O_4S_2$: C, 65.76; H, 6.18; S, 14.04. Found: C, 65.69; H, 6.21; S, 13.78.

(*Z*)-2,3-Bis(phenylseleno)-2-propenyl 2-propenyl ether (Table IV, entry 18): oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.92 (d, 2 H, J = 5.4 Hz), 4.03 (s, 2 H), 5.13 (d, 1 H, J = 10.3 Hz), 5.20 (d, 1 H, J = 17.0 Hz), 5.83 (octet, 1 H, J = 5.4, 10.3, 17.0 Hz), 7.26–7.31 (m, 6 H), 7.40 (s, 1 H), 7.55–7.60 (m, 4 H) (NOE experiment: Irradiation of the methylene singlet at δ 4.03 resulted in a 13% enhancement of the signal at δ 7.40 (vinyl singlet)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 70.96, 74.16, 117.08, 127.33, 127.57, 128.88, 129.15, 129.23, 130.51, 132.55 (J_{Se-C} = 12.0 Hz), 132.87 (J_{Se-C} = 12.0 Hz) 133.05, 134.30; IR (NaCl) 3056, 2846, 1577,

1476, 1438, 1099, 1022, 736, 690 cm^{-1}; mass spectrum (EI), *m/e* 410 (M^+, 26). Anal. Calcd for $C_{18}H_{18}OSe_2$: C, 52.96; H, 4.44. Found: C, 52.90; H, 4.72.

Reaction of 6 with 1-Octyne (1a). In a Pyrex NMR glass tube were placed $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), $(PhS)_2$ (4.4 mg, 0.02 mmol), and C_6D_6 (0.6 mL). When the mixture was heated at 65 °C for 2 h, the complete disappearance of $(PhS)_2$ was confirmed by ^{13}C NMR spectroscopy. 1-Octyne (**1a**) (3.0 mg, 0.027 mmol) was then added to this reaction mixture, and the mixture was heated at 65 °C for 15 h. As a result, the formation of 1,2-bis(phenylseleno)-1-octene (**3a**) was confirmed in 65% yield by ^1H NMR spectroscopy.

Palladium-Catalyzed Carbonylative Addition of $(PhSe)_2$ to 1-Octyne (1a) in an Atmosphere of Carbon Monoxide (Eq 6). To a two-necked 5-mL reaction vessel equipped with a magnetic stirring bar were added diphenyl diselenide (314 mg, 1.0 mmol), $Pd(PPh_3)_4$ (24 mg, 0.02 mmol), toluene (2.0 mL), and 1-octyne (**1a**) (110 mg, 1.0 mmol). The mixture was heated at 80 °C for 19 h under an atmosphere of carbon monoxide. The reaction mixture was filtered through Celite and evaporated in vacuo. The formation of (*Z*)-1,3-bis(phenylseleno)-2-nonen-1-one (**5a**) (29%) and (*Z*)-1,2-bis(phenylseleno)-1-octene (**3a**) (29%) was confirmed by ^1H NMR spectroscopy.

Palladium-Catalyzed Carbonylative Addition: General Procedure (Tables V and VI). 1,3-Bis(phenylthio)-2-nonen-1-one (4a) (Table VI, Entry 2). In a 50-mL stainless steel autoclave were placed diphenyl disulfide (218 mg, 1.0 mmol), $Pd(PPh_3)_4$ (24 mg, 0.02 mmol), benzene (0.5 mL), and 1-octyne (**1a**) (110 mg, 1.0 mmol). The mixture was heated at 80 °C for 15 h under pressure of carbon monoxide (60 kg/cm^2) with magnetic stirring. The reaction mixture was filtered through Celite and evaporated in vacuo. The residual mixture was purified by MPLC and PTLC to provide 298 mg (85%) of (*Z*)-1,3-bis(phenylthio)-2-nonen-1-one as a clear oil. *Z* isomer: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.80 (t, 3 H, J = 6.8 Hz), 0.97–1.06 (m, 4 H), 1.15 (m, 2 H), 1.34 (m, 2 H), 2.09 (t, 2 H, J = 5.4 Hz), 6.25 (s, 1 H), 7.35–7.53 (m, 10 H) (NOE experiment: Irradiation of the C-4 methylene triplet at δ 2.09 resulted in a 7% enhancement of the signal at δ 6.25 (vinyl singlet). The regiochemistry was determined from the result of the reduction of **4a** with an equimolar amount of *n*-Bu_3SnH in benzene-d_6 (the formyl doublet (J = 8.1 Hz) appeared at δ 10.15)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.90, 22.27, 28.43, 29.36, 31.12, 36.48, 116.93, 128.24, 128.97, 129.02, 129.07, 129.48, 130.31, 134.65, 135.79, 162.14, 184.96; IR (NaCl) 2926, 1671, 1548, 1476, 1439, 1085, 828, 745, 706, 690 cm^{-1}; mass spectrum (CI), *m/e* 357 (M^+ + 1, 100). Anal. Calcd for $C_{21}H_{24}OS_2$: C, 70.74; H, 6.78. Found: C, 70.88; H, 6.78.

E isomer: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, 3 H, J = 6.7 Hz), 1.20–1.42 (m, 6 H), 1.62 (quintet, 2 H, J = 7.6 Hz), 2.77 (t, 2 H, J = 7.8 Hz), 5.47 (s, 1 H), 7.35 (m, 5 H), 7.47–7.52 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.03, 22.54, 29.14, 29.80, 32.52, 34.49, 115.50, 128.56, 129.03, 129.09, 129.15, 129.87, 130.10, 134.59, 135.50, 165.64, 183.90; IR (NaCl) 3060, 2928, 1679. 1567, 1440, 1340, 1046, 841, 746, 708 cm^{-1}; mass spectrum (CI), *m/e* 357 (M^+ + 1, 100).

The solvent (hexane/Et_2O) was used as eluent in the following ratios: 10:1 (entries 1–6 in Table V and entries 1–9 in Table VI), 4:1 (entry 10), 1:1 (entry 11). Dichalcogen compounds, the pressure of carbon monoxide, catalyst, reaction time, and yields are listed in the Tables V and VI. The following compounds were prepared according to the general procedure.

1,3-Bis(phenylseleno)-2-nonen-1-one (5a) (Table V). *Z* isomer: mp 35–39 °C (a light yellow crystal); ^1H NMR (270 MHz, $CDCl_3$) δ 0.81 (t, 3 H, J = 7.2 Hz), 1.01 (m, 4 H), 1.14 (m, 2 H), 1.31 (m, 2 H), 2.13 (t, 2 H, J = 7.8 Hz), 6.66 (s, 1 H, J_{Se-H} = 12.5 Hz), 7.31–7.44 (m, 6 H), 7.57–7.65 (m, 4 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.13 resulted in a 20% enhancement of the signal at δ 6.66 (vinyl singlet). The regiochemistry was determined from the result of the reduction of **5a** with an equimolar amount of *n*-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 9.88 (J = 3.8 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.96, 22.32, 28.44, 29.78, 31.17, 37.77, 121.98, 126.70, 127.30, 128.81, 129.15, 129.29, 129.34, 135.83 (J_{Se-C} = 9.4 Hz), 137.32 (J_{Se-C} = 10.7 Hz), 163.13, 187.58; IR (KBr) 3081, 2928, 2855, 1671, 1539, 1438, 1092, 801, 738, 688 cm^{-1}; mass spectrum (CI), *m/e* 453 (M^+ + 1, 68). Anal. Calcd for $C_{21}H_{24}OSe_2$: C, 56.00; H, 5.37. Found: C, 55.98; H, 5.70.

E isomer: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, 3 H, J = 6.6 Hz), 1.19–1.38 (m, 6 H), 1.55 (m, 2 H), 2.76 (t, 2 H, J = 7.8 Hz), 5.82 (s, 1 H), 7.32–7.46 (m, 8 H), 7.57–7.60 (m, 2 H) (the regiochemistry was determined from the result of the reduction of **5a** with an equimolar amount of *n*-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 9.74 (J = 7.6 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.04, 22.53, 29.06, 29.90, 31.49, 35.89 (J_{Se-C} = 22.0 Hz), 122.41 (J_{Se-C} = 61.6 Hz), 126.29, 127.19, 128.69, 129.24, 129.77, 129.96, 135.71 (J_{Se-C} = 8.5 Hz), 136.74 (J_{Se-C} = 10.4 Hz), 164.50, 185.76; IR (NaCl) 3057, 2927, 1694, 1563, 1557, 1476, 1438, 1020, 736, 689 cm^{-1}; mass spectrum (CI), *m/e* 453 (M^+ + 1, 44). Anal. Calcd for $C_{21}H_{24}OSe_2$: C, 56.00; H, 5.37. Found: C, 56.17; H, 5.66.

1,3-Bis[(*p*-methylphenyl)thio]-2-nonen-1-one (Table VI, Entry 4). *Z* isomer: mp 49–49.5 °C (a white solid); ^1H NMR ($CDCl_3$, 270 MHz) δ 0.81 (t, 3 H, J = 7.1 Hz), 1.04 (m, 4 H), 1.16 (m, 2 H), 1.34 (m, 2 H), 2.09 (t, 2 H, J = 7.6 Hz), 2.36 (s, 6 H), 6.23 (s, 1 H), 7.14–7.22 (m, 4 H), 7.35–7.40 (m, 4 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.09 resulted in a 14% enhancement of the signal at δ 6.23 (vinyl singlet). The regiochemistry was determined from the result of the reduction with an equimolar amount of *n*-Bu_3SnH in benzene-d_6 (the two formyl doublets appeared at δ 9.79 (J = 7.0 Hz) and δ 10.43 (J = 7.0 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.92, 21.20, 21.25, 22.29, 28.43, 29.37, 31.16, 36.35, 116.72, 124.83, 126.87, 129.78, 129.78, 134.61, 135.70, 139.23, 139.69, 162.50, 185.34; IR (KBr) 2928, 1669, 1545, 1492, 1104, 1087, 831, 809, 796 cm^{-1}; mass spectrum (CI), *m/e* 385 (M^+ + 1, 77). Anal. Calcd for $C_{23}H_{28}OS_2$: C, 71.82; H, 7.33; S, 16.67. Found: C, 71.78; H, 7.43; S, 16.71.

E isomer (this isomer was obtained by the reaction using $Pd(PPh_3)_2Cl_2$ as a catalyst (81%, E/Z = 5/95)) (not shown in Table VI): oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.87 (t, 3 H, J = 6.8 Hz), 1.26–1.37 (m, 6 H), 1.59–1.64 (m, 2 H), 2.35 (s, 3 H), 2.42 (s, 3 H), 2.76 (t, 2 H, J = 7.8 Hz), 5.47 (s, 1 H), 7.18 (d, 2 H, J = 8.3 Hz), 7.25 (d, 2 H, J = 8.3 Hz), 7.31 (d, 2 H, J = 8.3 Hz), 7.39 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$), δ 14.08, 21.35, 21.44, 22.59, 29.21, 29.88, 31.58, 34.51, 115.29, 125.12, 125.64, 129.91, 130.68, 134.64, 135.44, 139.34, 140.45, 165.96, 184.40; IR (NaCl) 2955, 2926, 1679, 1568, 1493, 1044, 1018, 808, 688 cm^{-1}; mass spectrum (CI), *m/e* 385 (M^+ + 1, 100); exact mass (M^+) calcd for $C_{23}H_{28}OS_2$ 384.1581, found 384.1593.

(*Z*)-1,3-Bis[(*p*-methylphenyl)seleno]-2-nonen-1-one (Table VI, entry 5): oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.80 (t, 3 H, J = 7.08 Hz), 0.98–1.03 (m, 4 H), 1.14 (m, 2 H), 1.31 (quintet, 2 H, J = 7.6 Hz), 2.12 (t, 2 H, J = 7.6 Hz), 2.35 (s, 3 H), 2.36 (s, 3 H), 6.64 (s, 1 H, J_{Se-H} = 12.7 Hz), 7.13 (d, 2 H, J = 7.8 Hz), 7.19 (d, 2 H, J = 8.3 Hz), 7.45 (d, 2 H, J = 8.3 Hz), 7.49 (d, 2 H, J = 7.8 Hz) (NOE experiment: Irradiation of the methylene triplet at δ 2.12 resulted in a 19% enhancement of the signal at δ 6.64 (vinyl singlet). The regiochemistry was determined from the result of the reduction with an equimolar amount of *n*-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 9.88 (J = 3.9 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.00, 21.29, 21.32, 22.35, 28.45, 29.78, 31.21, 37.65, 121.92, 123.22, 123.85, 129.95, 130.15, 135.85 (J_{Se-C} = 9.5 Hz), 137.23 (J_{Se-C} = 9.5 Hz), 138.86, 139.46, 163.36, 187.91; IR (NaCl) 3018, 2954, 2926, 2857, 1667, 1538, 1489, 1090, 803 cm^{-1}; mass spectrum (CI), *m/e* 481 (M^+ + 1, 21). Anal. Calcd for $C_{23}H_{28}OSe_2$: C, 57.74; H, 5.89. Found: C, 57.76; H, 6.11.

(*Z*)-1,3-Bis[[(*p*-trifluoromethyl)phenyl]seleno]-2-nonen-1-one (Table VI, entry 6): oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.80 (t, 3 H, J = 7.1 Hz), 1.02 (m, 4 H), 1.15 (m, 2 H), 1.34 (m, 2 H), 2.15 (t, 2 H, J = 7.8 Hz), 6.69 (s, 1 H, J_{Se-H} = 16 Hz), 7.61 (d, 2 H, J = 7.8 Hz), 7.64 (d, 2 H, J = 7.8 Hz), 7.71 (d, 2 H, J = 7.8 Hz), 7.78 (d, 2 H, J = 7.8 Hz) (NOE experiment: Irradiation of the methylene triplet at δ 2.15 resulted in a 21% enhancement of the signal at δ 6.69 (vinyl singlet). The regiochemistry was determined from the result of the reduction with an equimolar amount of *n*-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 9.72 (J = 2.9 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.88, 22.33, 28.41, 29.76, 31.15, 37.97, 122.36, 123.78 (q, J = 272 Hz), 123.98 (q, J = 272 Hz), 125.99 (q, J = 2.9 Hz), 126.05 (q, J = 2.9 Hz), 130.93 (q, J = 33 Hz), 131.17, 131.69 (q, J = 33 Hz), 131.78, 135.86, 137.62, 162.52, 186.36; IR (NaCl) 2958, 2931, 2859, 1666, 1602, 1540, 1324, 1168, 1130, 1101, 1076, 1058, 1014, 832 cm^{-1}; mass spectrum (CI), *m/e* 589 (M^+ + 1, 71). Anal. Calcd for $C_{23}H_{22}F_6OSe_2$: C, 47.11; H, 3.78. Found: C, 47.34; H, 3.86.

(*Z*)-1,3-Bis(phenylseleno)-6-methyl-2-hepten-1-one (Table VI, entry 7): mp 83–84 °C (a light yellow crystal); ^1H NMR (270 MHz, $CDCl_3$) δ 0.60 (d, 6 H, J = 6.1 Hz), 1.20–1.24 (m, 3 H), 2.15 (t, 2 H, J = 7.6 Hz), 6.66 (s, 1 H, J_{Se-H} = 14.0 Hz), 7.31–7.40 (m, 6 H), 7.57–7.65 (m, 4 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.15 resulted in a 10% enhancement of the signal at δ 6.66 (vinyl singlet). The regiochemistry was determined from the result of the reduction with an equimolar amount of *n*-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 9.84 (J = 3.5 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.99, 27.66, 35.91, 39.07, 121.06, (J_{Se-C} = 58.0 Hz), 126.78, 127.35, 128.81, 129.18, 129.30, 129.40, 135.34 (J_{Se-C} = 9.0 Hz), 137.41 (J_{Se-C} = 10.0 Hz), 163.39, 187.49; IR (KBr) 3053, 2953, 2870, 1672, 1662, 1540, 1438, 1093, 804, 741, 690 cm^{-1}; mass spectrum (CI), *m/e* 439 (M^+ + 1, 44). Anal. Calcd for $C_{20}H_{22}OSe_2$: C, 55.05; H, 5.08. Found: C, 55.15; H, 5.10.

1,3-Bis(phenylseleno)-3-phenyl-2-propen-1-one (Table VI, Entry 8). *Z* isomer: mp 135–141 °C (a yellow crystal); ^1H NMR (270 MHz, $CDCl_3$) δ 6.80 (s, 1 H), 6.95–7.08 (m, 8 H), 7.19 (d, 2 H, J = 6.8 Hz),

7.40–7.42 (m, 3 H), 7.60–7.62 (m, 2 H) (The regiochemistry was determined from the result of the reduction with an equimolar amount of n-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 10.06 (J = 4.9 Hz))); ^{13}C NMR (270 MHz, $CDCl_3$) δ 124.73, 126.66, 127.57, 128.09, 128.33, 128.45, 128.67, 128.93, 129.05, 129.37, 135.79, 136.05, 138.58, 159.57, 187.77; IR (KBr) 3057, 1658, 1531, 1486, 1476, 1437, 1227, 1042, 935, 760, 744, 696 cm^{-1}; mass spectrum (CI), m/e 445 (M^+ + 1, 56). Anal. Calcd for $C_{21}H_{16}OSe_2$: C, 57.03; H, 3.64. Found: C, 57.19; H, 3.64.

E isomer: Pure E isomer could not be isolated because it was formed in low yield.

1,3-Bis(phenylthio)-3-phenyl-2-propen-1-one (Table VI, Entry 9). Z isomer: mp 135–139 °C (a yellow solid); ^1H NMR (270 MHz, $CDCl_3$) δ 6.45 (s, 1 H), 7.03–7.13 (m, 10 H), 7.43–7.44 (m, 3 H), 7.52–7.53 (m, 2 H) (The regiochemistry was determined from the result of the reduction with an equimolar amount of n-Bu_3SnH in benzene-d_6 (the two formyl doublets appeared at δ 9.50 (J = 8.1 Hz) and δ 10.47 (J = 6.5 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 121.02, 127.83, 128.01, 128.11, 128.43, 128.66, 128.93, 129.14, 129.32, 132.06, 134.17, 134.67, 137.74, 158.63, 185.19; IR (KBr) 3059, 1661, 1537, 1078, 949, 791, 752, 705, 690, 671, 588 cm^{-1}; mass spectrum (CI), m/e 349 (M^+ + 1, 100). Anal. Calcd for $C_{21}H_{16}OS_2$: C, 72.38; H, 4.62; S, 18.40. Found: C, 72.37; H, 4.61; S, 18.32.

E isomer: Pure E isomer could not be isolated because it was formed in low yield.

(Z)-1,3-Bis(phenylseleno)-5,5-bis(ethoxycarbonyl)-2,7-octadien-1-one (Table VI, entry 10): mp 66–68 °C (a light yellow crystal); ^1H NMR (270 MHz, $CDCl_3$) δ 1.22 (t, 6 H, J = 7.1 Hz), 2.54 (d, 2 H, J = 8.3 Hz), 2.80 (s, 2 H), 4.15 (q, 4 H, J = 7.1 Hz), 4.88 (d, 1 H, J = 20.5 Hz), 4.93 (d, 1 H, J = 14.0 Hz), 5.35 (octet, 1 H, J = 8.3, 14.0, 20.5 Hz), 6.74 (s, 1 H), 7.34–7.46 (m, 6 H), 7.55–7.60 (m, 4 H) (NOE experiment: Irradiation of the methylene singlet at δ 2.80 resulted in an 11% enhancement of the signal at δ 6.74 (vinyl singlet). The regiochemistry was determined from the result of the reduction with an equimolar amount of n-Bu_3SnH in benzene-d_6 (the two formyl doublets appeared at δ 9.74 (J = 7.6 Hz) and δ 9.96 (J = 4.9 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.07, 38.17, 38.60, 58.02, 61.76, 119.38, 124.52, 126.63, 127.75, 128.92, 129.37, 129.41, 129.50, 131.92, 135.76, 137.22, 155.35, 170.06, 187.45; IR (KBr) 3053, 2982, 1730, 1669, 1543, 1219, 1066, 793, 744, 693 cm^{-1}; mass spectrum (CI), m/e 581 (M^+ + 1, 14). Anal. Calcd for $C_{26}H_{28}O_5Se_2$: C, 53.98; H, 4.87. Found: C, 54.23; H, 4.90.

1,3-Bis(phenylseleno)-6-hydroxy-2-hexen-1-one (Table VI, Entry 11). Z isomer: mp 98–100 °C (a light yellow crystal); ^1H NMR (270 MHz, $CDCl_3$) δ 1.55 (quintet, 2 H, J = 6.1, 7.6 Hz), 1.70 (br s, 1 H), 2.26 (t, 2 H, J = 7.6 Hz), 3.29 (t, 2 H, J = 6.1 Hz), 6.71 (s, 1 H, J_{Se-H} = 11.7 Hz), 7.30–7.65 (m, 10 H) (NOE experiment: Irradiation of the methylene triplet at δ 2.26 resulted in a 21% enhancement of the signal at δ 6.71 (vinyl singlet). The regiochemistry was determined from the result of the reduction with an equimolar amount of n-Bu_3SnH in benzene-d_6 (the formyl doublet appeared at δ 9.81 (J = 3.9 Hz))); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.35, 33.99, 61.06, 122.49, 126.58, 127.08, 128.83, 129.24, 129.29, 129.45, 135.74, 137.23, 161.95, 187.69; IR (KBr) 3326, 3055, 2937, 1664, 1546, 1532, 1085, 809, 742, 693 cm^{-1}; mass spectrum (CI), m/e 427 (M^+ + 1, 8). Anal. Calcd for $C_{18}H_{18}O_2Se_2$: C, 50.96; H, 4.27. Found: C, 51.01; H, 4.34.

E isomer: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 1.87 (quintet, 2 H, J = 5.9, 7.3 Hz), 2.07 (br s, 1 H), 2.88 (t, 2 H, J = 7.3 Hz), 3.62 (t, 2 H, J = 5.9 Hz), 5.94 (s, 1 H), 7.30–7.66 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 31.69, 32.55, 61.09, 123.48, 126.03, 126.87, 128.88, 129.32, 129.94, 130.07, 135.69 (J_{Se-C} = 8.8 Hz), 136.72, 163.43, 187.74; IR (NaCl) 3368, 3056, 2942, 2874, 1693, 1564, 1557, 1476, 1438, 1338, 1038, 1020, 738, 690 cm^{-1}; mass spectrum (CI), m/e 427 (M^+ + 1, 8).

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An Approach to Organic Ferromagnets. Synthesis and Characterization of 1-Phenyl-1,3-butadiyne Polymers Having a Persistent Nitroxide Group on the Phenyl Ring

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Abstract: 1-[3-(*N-tert*-Butylhydroxyamino)-4-chlorophenyl]-1,3-butadiyne (**3**) was obtained as colorless needles (mp ca. 140 °C from diethyl ether) that polymerized 100% in 24 h at 120 °C to give a black, ethanol-insoluble microcrystalline product. Crystals of **3** are triclinic, space group $P\bar{1}$ (No. 2), with a = 8.496 (3) Å, b = 10.755 (5) Å, c = 8.004 (3) Å, α = 92.77 (4)°, β = 106.51 (3)°, γ = 74.85 (3)°, V = 676.6 (5) Å^3, and d = 1.22 g/cm^3 for Z = 2 ($C_{14}H_{14}ClON$, MW = 247.72). The observed solid-state polymerization is estimated to have taken place along the a/c diagonal. Treatment of **3** with Fremy's salt in THF/H_2O at room temperature gave the corresponding nitroxide radical **4** as red crystals (mp 81.0–82.0 °C, a_N = 13.8 G, g = 2.0066 in hexane). Whereas the planned solid-state polymerization of **4** proceeded neither by heat nor UV and γ irradiation, mixed crystals of **3** and **4** (70:30 to 50:50) did undergo polymerization in 20 h at 140 °C to give a black, ethanol-insoluble solid. A broad X-band ESR signal that showed geometrical anisotropy was observed at ca. 3000 G in addition to resonances at g = 2 due to the isolated ($S = {}^1/_2$) and exchange-narrowed nitroxide spins. The magnetic susceptibility of the polymer samples measured on a Faraday balance showed that ca. 90% of the nitroxide radical centers were lost during the polymerization. Most of the remaining spins are $S = {}^1/_2$, and the rest are in a segment where $S > {}^1/_2$. The latter spins were found to be quenched by an anomalous phase transition at ca. 250 K when the samples were warmed up from cryogenic temperatures.

The design and synthesis of organic magnets are the subject of increasing current interest.[1] The idea is to establish unprecedented macroscopic spins of long-range order in molecular systems. There appear to be two approaches for the purpose: spin alignment within a molecule and between neighboring molecules. The pros and cons of the two approaches have been discussed.[2] The former approach was highlighted by the synthesis and

(1) (a) Itoh, K. *Bussei* **1971**, *12*, 635. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40. (c) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114. (d) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (e) Miller, J. S.; Kruisic, P. J.; Epstein, A. J.; Zhang, J. H.; Dixon, D. D.; Calabrese, J. C. *Science* **1988**, *240*, 1185. (f) Iwamura, H. *Oyo Butsuri* **1989**, *58*, 1061–8. (g) Buchachenko, A. L. *Usp. Khim.* **1990**, *59*, 307. (h) Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 2764.

(2) (a) Iwamura, H.; Izuoka, A. *Nippon Kagaku Kaishi* **1987**, 595. (b) Iwamura, H. *J. Phys. (Paris)* **1988**, *49*, C8 813. (c) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

0002-7863/91/1513-9803$02.50/0