Selected Papers

Transition-Metal-Catalyzed Cyanochalcogenation of Alkynes with Chalcogenocyanates

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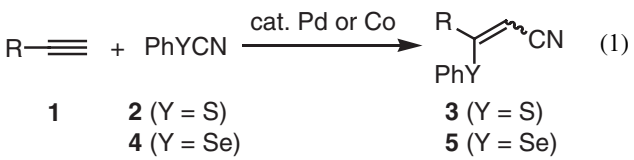
Tetrakis(triphenylphosphine)palladium(0) catalyzes the highly regioselective addition of phenyl thiocyanate to terminal alkynes, which attains the simultaneous introduction of thio and cyano groups into the internal and terminal positions of alkynes, respectively. In addition, dicobalt octacarbonyl indicates moderate catalytic activity toward the same cyanothiolation of alkynes with excellent regioselectivity. By using $[Co_2(CO)_8]$ as the catalyst, novel cyanoselenation of alkynes with phenyl selenocyanate has also been attained in moderate yield with excellent regioselectivity.

The transition-metal-catalyzed reactions of organoboron, organosilicon, and organotin compounds are utilized widely in organic synthesis.[1] In contrast, the transition-metal-catalyzed reactions of group 16 compounds had been largely unexplored, partly because these compounds were believed to be catalyst poisons for a variety of transition-metal-catalyzed reactions.[2] Recently, synthetically useful transition-metal-catalyzed reactions of organosulfur compounds have been developed.[3] A series of transition-metal-catalyzed addition reactions of organosulfur and organoselenium compounds have been disclosed, e.g., highly selective bisthiolation,[4] hydrothiolation,[5] and thiocarbonylation[5d,6] of unsaturated compounds such as alkynes (and the corresponding reactions of selenium analogs[7]). These reactions clearly demonstrate that the transition-metal catalysts are indeed effective for the highly selective synthetic reactions of organosulfur and organoselenium compounds based on the cleavage of heteroatom–heteroatom and heteroatom–hydrogen bonds. However, the introduction of sulfur groups to carbon–carbon unsaturated compounds based on the sulfur–carbon bond cleavage by the transition-metal catalysts is still rare.[8] Herein we report highly regioselective cyanothiolation and cyanoselenation of terminal alkynes with thio- and selenocyanates in the presence of transition-metal catalysts (eq 1).[9–11]



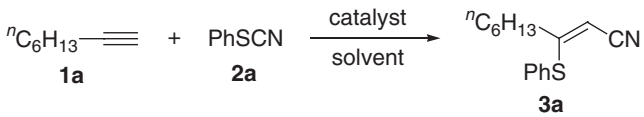
(1)

1 **2** (Y = S) **4** (Y = Se) **3** (Y = S) **5** (Y = Se)

Results and Discussion

The reaction of phenyl thiocyanates with 1-octyne (**1a**) was examined in the presence of several transition-metal catalysts (Table 1). While $PdCl_2$, $[Pd_2(dba)_3]$ (dba: dibenzylideneacetone), $NiCl_2$, $[Pt(PPh_3)_4]$, $CoCl_2$, and $[RhH(CO)(PPh_3)_3]$ catalysts indicated no catalytic activity (Entries 1, 3–6, and 8), low-valent complexes of palladium and cobalt such as $[Pd(PPh_3)_4]$ and $[Co_2(CO)_8]$ indicated catalytic activity toward the desired cyanothiolation of 1-octyne (Entries 2 and 7). Although the yields of the cyanothiolation product were low in these $[Pd(PPh_3)_4]$- and $[Co_2(CO)_8]$-catalyzed reactions, excellent regioselectivity was observed: thio and cyano groups were introduced into the internal and terminal positions of 1-octyne, regioselectivity.

Table 1. Catalytic Activity of Transition-Metal Complexes on the Reaction of 1-Octyne with PhSCN[a)]



1a **2a** **3a**

Entry	Catalyst	Solvent	Temp/°C	Time/h	Yield/%[b)]
1	$PdCl_2$	benzene	140	62	0
2	$[Pd(PPh_3)_4]$	toluene	110	60	16
3	$[Pd_2(dba)_3]$	benzene	140	62	trace
4	$NiCl_2$	CH_3CN	120	65	0
5	$[Pt(PPh_3)_4]$	benzene	120	20	0
6[c)]	$CoCl_2$	CH_3CN	140	41	0
7	$[Co_2(CO)_8]$	CH_2Cl_2	140	71	14
8	$[RhH(CO)(PPh_3)_3]$	CH_3CN	140	67	0

a) Reaction conditions: catalyst (10 mol %), **1a** (1.0 mmol), **2a** (1.0 mmol), solvent (1 mL). b) Determined by ^{1}H NMR. c) $CoCl_2$ (5 mol %).

To optimize the reaction conditions, a series of $[Co_2(CO)_8]$-catalyzed reactions of 1-octyne (**1a**) with phenyl thiocyanate was carried out under various conditions (Table 2). Interestingly, the yield of the desired cyanothiolation product **3a** was improved when the reaction was carried out in the presence of carbon monoxide: in the absence of carbon monoxide, the yield of **3a** was 14%, whereas the yield was improved up to 45% in

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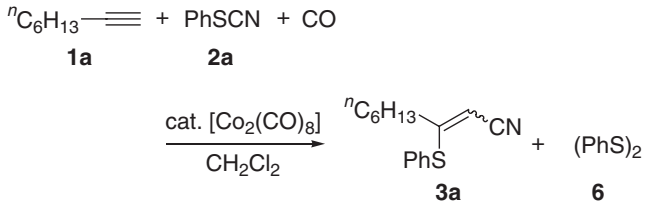
Table 2. $[Co_2(CO)_8]$-Catalyzed Addition of PhSCN to 1-Octyne in the Presence of CO[a)]

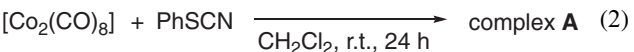


Entry	Additive	Temp /°C	Time /h	Yield/%[b)] [E/Z] 3a	6
1[c)]		120	11	7 [0/100]	0
2[d)]		120	84	34 [0/100]	56
3[e)]		140	71	14 [0/100]	trace
4		140	60	45 [9/91]	55
5	$(PhS)_2$ (30 mol %)	140	72	31 [45/55]	24
6	PPh_3 (20 mol %)	140	68	16 [trace/100]	—[f)]
7		160	84	50 [78/22]	37

a) Reaction conditions: $[Co_2(CO)_8]$ (10 mol %), **1a** (1.0 mmol), **2a** (1.0 mmol), CH_2Cl_2 (1 mL), CO (3 MPa). b) Determined by ^{1}H NMR. c) **1a** (3 mmol). d) **2a** (1.5 mmol). e) In the absence of CO. f) Not determined.

the presence of 3 MPa of carbon monoxide (Entries 3 and 4).[12] The addition of diphenyl disulfide or phosphine to the catalytic system did not improve the yield of **3a** (Entries 5 and 6). The reaction of 1-octyne with 1 equivalent of phenyl thiocyanate (**2a**) at higher temperature (160 °C) provided the desired cyanothiolation product **3a** in 50% yield along with 37% yield of diphenyl disulfide (Entry 7). In this case, the *E*-isomer was formed predominantly. Since the *Z*-isomer was obtained predominantly at lower temperature (120–140 °C), the *Z*-isomer might isomerize to *E*-isomer at higher temperature (160 °C).[13] In this $[Co_2(CO)_8]$-catalyzed cyanothiolation, diphenyl disulfide was formed as a by-product abundantly.

To get insight into the reaction pathway for the $[Co_2(CO)_8]$-catalyzed cyanothiolation, the stoichiometric reaction of $[Co_2(CO)_8]$ with PhSCN was examined (eq 2). The equimolar reaction of $[Co_2(CO)_8]$ with PhSCN at room temperature in CH_2Cl_2 under an argon atmosphere afforded a black solid (complex **A**). The IR spectra of complex **A** showed bridged and terminal coordinated CO absorptions at 1854, 2036, and 2098 cm^{-1} and CN absorption at 2137 cm^{-1}. From this result and elemental analysis, it is assumed that complex **A** has a cluster structure bridged by carbonyl, thio or cyano groups. Furthermore, the catalytic reaction of 1-octyne with PhSCN in the presence of complex **A** was examined and the reaction afforded the cyanothiolation product **3a** in 35% yield (eq 3).



Anal. Calcd for $[Co_2(CO)_2(CN)(SPh)]$:
C, 34.97; H, 1.63; N, 4.53%.
Found: C, 35.03; H, 1.63; N, 4.53%.
mp: >300 °C IR: 1854, 2036, 2098 cm^{-1} (CO) 2137 cm^{-1} (CN)

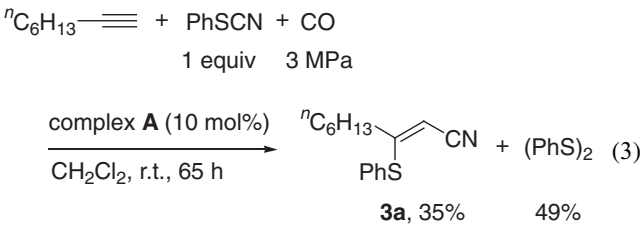
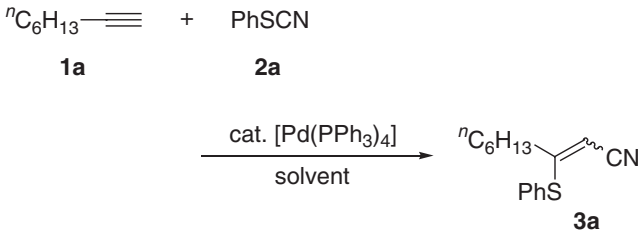


Table 3. Influence of Solvents on the $[Pd(PPh_3)_4]$-Catalyzed Cyanothiolation[a)]



Entry	Solvent	Temp/°C	Time/h	Yield/%[b)]	[E/Z]
1	benzene	120	66	61	[trace/≈100]
2	toluene	120	66	44	[trace/≈100]
3	xylene	120	66	34	[trace/≈100]
4	THF	120	66	42	[trace/≈100]
5	CH_3CN	120	66	12	[trace/≈100]
6	benzene	80	24	9	[trace/≈100]
7	benzene	120	24	12	[trace/≈100]
8	benzene	140	66	56	[12/88]

a) Reaction conditions: $[Pd(PPh_3)_4]$ (10 mol %), **1a** (1.0 mmol), **2a** (1.0 mmol), solvent (1 mL). b) Determined by ^{1}H NMR.

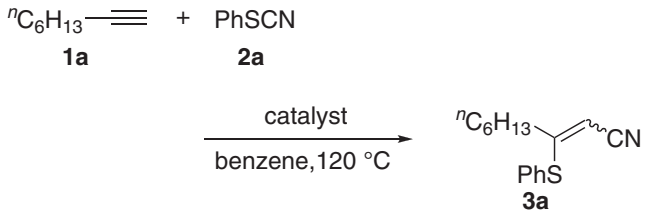
Next, the $[Pd(PPh_3)_4]$-catalyzed cyanothiolation was investigated under various reaction conditions. To optimize the reaction conditions at first, the $[Pd(PPh_3)_4]$-catalyzed reaction of 1-octyne with phenyl thiocyanate was examined under several reaction conditions (Table 3). The reaction was greatly influenced by the solvent employed. Among the solvents employed (benzene, toluene, xylene, THF, and CH_3CN), benzene was suitable for the present reaction to afford higher yields of **3a**, whereas the reaction in CH_3CN resulted in the low yield of **3a** (Entries 1–5). When the cyanothiolation was conducted at lower temperature (80 °C) or for shorter reaction time (24 h), the reaction gave **3a** in only 9% and 12% yields, respectively (Entries 6 and 7). Prolonged reaction time led to a great increase in yield (Entry 1). Higher temperature (140 °C) led to the formation of **3a** in 56% yield (Entry 8). Consequently, upon heating at 120 °C in benzene, the desired cyanothiolation product **3a** was obtained in good yield with excellent regioselectivity (Entry 1).

In the presence of several palladium catalysts, the cyanothiolation of 1-octyne with phenyl thiocyanate was examined, and the results are summarized in Table 4. Pd(0) complex as $[Pd(PPh_3)_4]$ was the most effective catalyst toward this cyanothiolation (Entry 1).[14] When the $[Pd(PPh_3)_4]$-catalyzed reaction in the presence of carbon monoxide was conducted, the yield of the cyanothiolation product decreased (25%) and thioester **3a′**, which is the carbonylative addition product of diphenyl disulfide, was obtained in 18% yield (Entry 2). The addition of phosphines such as triphenylphosphine and diphenylphosphinopropane (DPPP) to palladium acetate re-

sulted in the decrease in the yield of **3a** (Entries 3 and 4). Pd(II) complex such as $PdCl_2$ exhibits no catalytic activity and the starting materials were recovered unchanged (Entry 5).

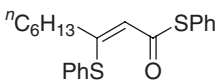
By using the optimized reaction conditions (Table 4, Entry 1), we next examined the $[Pd(PPh_3)_4]$-catalyzed cyanothiolation of some other terminal alkynes, and the results are shown in Table 5. 5-Methyl-1-hexyne and 5-cyano-1-pentyne underwent the regio- and stereoselective cyanothiolation, affording the corresponding adducts in good yields (Entries 1 and 2). 1-Ethynylcyclohexene regioselectively provided the conjugated cyanothiolation product as a stereoisomeric mixture (Entry 4). The cyanothiolation of aromatic alkynes such as phenylacetylene in benzene gave low yield (35%) of the desired product; however, a similar reaction in the absence of benzene led to the increase in the yield (84%, Entry 5). Similarly, the reaction of 4-ethynyltoluene in the absence of benzene afforded the cyanothiolation product in good yield (81%, Entry 6). In contrast to PhSCN, the addition of aliphatic thiocyanate such as *n*-butyl thiocyanate (*n*-BuSCN) resulted in poor yield of the adduct (9% yield).

Table 4. Cyanothiolation of 1-Octyne Catalyzed by Palladium Complexes[a)]



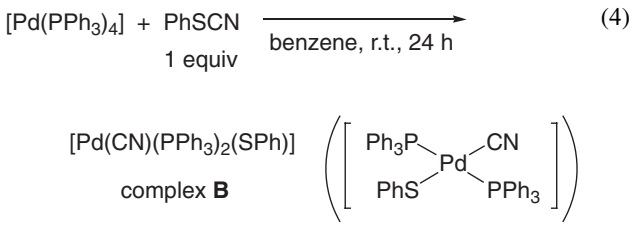
Entry	Catalyst	Additive	Time /h	Yield /%[b)]	[*E*/*Z*]
1	$[Pd(PPh_3)_4]$		66	61	[trace/≈100]
2[c)]	$[Pd(PPh_3)_4]$	CO (3 MPa)	66	25	[trace/≈100]
3	$Pd(OAc)_2$	PPh_3 (40 mol %)	73	47	[trace/≈100]
4	$Pd(OAc)_2$	DPPP (10 mol %)	66	10	[trace/≈100]
5[d)]	$PdCl_2$		62	0	

a) Reaction conditions: catalyst (10 mol %), **1a** (1.0 mmol), **2a** (1.0 mmol), benzene (1 mL). b) Determined by ^{1}H NMR. c) **1a** (3.0 mmol) was employed, and thioester **3a′** was obtained in 18% yield as a by-product. d) 140 °C.



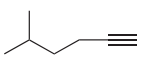
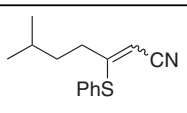
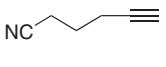
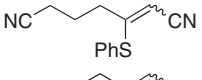
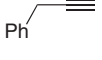
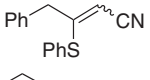
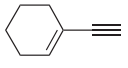
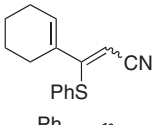
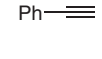
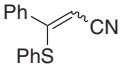
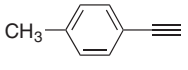
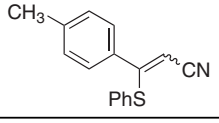
3a′

To get insight into the reaction pathway for this cyanothiolation, the equimolar reaction of $[Pd(PPh_3)_4]$ with PhSCN in benzene was conducted at room temperature to afford a yellow solid (complex **B**) (eq 4). The IR spectrum of complex **B** showed a CN absorption (2130 cm^{-1}). This and elemental analysis suggest that the structure of complex **B** can be assumed to be $[Pd(CN)(PPh_3)_2(SPh)]$. Furthermore, the X-ray crystal structure analysis clearly indicates that complex **B** is the mononuclear Pd(II) complex with *trans*-form, i.e., "*trans*-$[Pd(CN)(PPh_3)_2(SPh)]$" (for the X-ray analysis, see Ref. 9).[15,16]

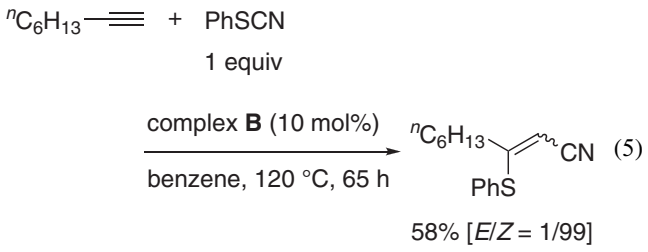


Anal. Calcd for $C_{43}H_{35}NP_2PdS$:
C, 67.41; H, 4.60; N, 1.83%.
Found: C, 68.19; H, 4.66; N, 1.97%.
mp: 229-230 °C IR: 2130 cm^{-1} (CN)

Table 5. $[Pd(PPh_3)_4]$-Catalyzed Cyanothiolation of Terminal Alkynes[a)]

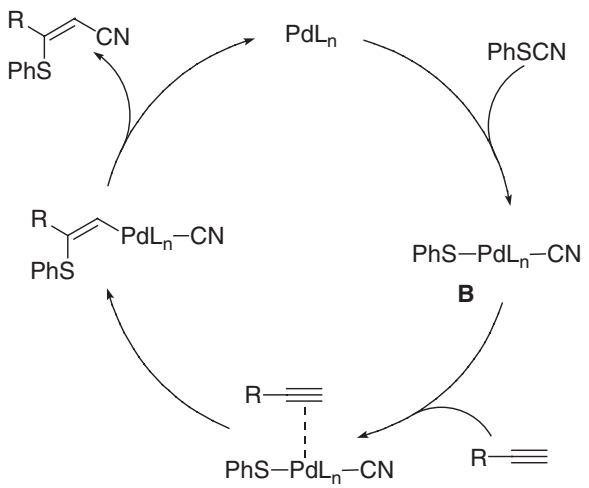
Entry	Alkyne		Product		Yield/%[b)]	[*E*/*Z*][c)]
1		**1b**		**3b**	60	[1/99]
2		**1c**		**3c**	48	[1/99]
3		**1d**		**3d**	53	[17/83]
4		**1e**		**3e**	56	[58/42]
5		**1f**		**3f**	84	[14/86]
6[d)]		**1g**		**3g**	81	[12/88]

a) Reaction conditions: $[Pd(PPh_3)_4]$ (10 mol %), alkyne (1.0 mmol), thiocyanate (1.0 mmol), benzene (Entries 1 and 2), without benzene (Entries 3–6), 120 °C, 66 h. b) Isolated yield. c) Determined by ^{1}H NMR. d) 20 h.



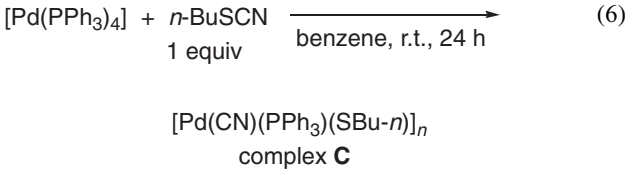
A catalytic reaction of 1-octyne with PhSCN was examined in the presence of complex **B** as the catalyst and the corresponding cyanothiolation product was obtained in 58% yield (eq 5).

Scheme 1 shows a possible reaction pathway on the basis of these results, which includes the following: (i) complex **B** is formed via oxidative addition of PhSCN to [Pd(PPh$_3$)$_4$] with the cleavage of sulfur–cyano bond; (ii) alkyne coordinates to complex **B**; (iii) *syn*-thiopalladation (or *syn*-cyanopalladation) of the alkyne forms (*Z*)-vinylpalladium intermediate; (iv) reductive elimination of the cyanothiolation product occurs with the retention of the stereochemistry along with regeneration of the catalyst.[10c,10d,17]



Scheme 1. A possible pathway for the [Pd(PPh$_3$)$_4$]-catalyzed cyanothiolation.

Next, the stoichiometric reaction of [Pd(PPh$_3$)$_4$] with aliphatic thiocyanate such as *n*-butyl thiocyanate was examined. The reaction of [Pd(PPh$_3$)$_4$] with 1 equivalent of *n*-BuSCN at room temperature in benzene under an argon atmosphere afforded a white solid (complex **C**) (eq 6). From the results of the elemental analysis and IR spectrum of complex **C**, it is assumed that complex **C** has the structure [Pd(CN)(PPh$_3$)(SBu-*n*)].



Anal. Calcd for $C_{23}H_{24}NPPdS$:
C, 57.09; H, 5.00; N, 2.89%.
Found: C, 57.24; H, 5.00; N, 2.92%.
mp: 240 °C (dec.); IR: 2131 cm^{-1} (CN)

We succeeded in the X-ray analysis of complex **C**, clearly indicating that complex **C** is a binuclear palladium(II) complex bridged by thio groups (Figure 1). Each palladium atom formed tetracoordinated complex and –SBu-*n* and –CN groups of the complex were located in the *cis*-position.

It should be noted that the substituent on thiocyanate largely affected the yield. In the case of an aromatic group on sulfur, lone pairs of electrons on sulfur conjugate with π-electrons of

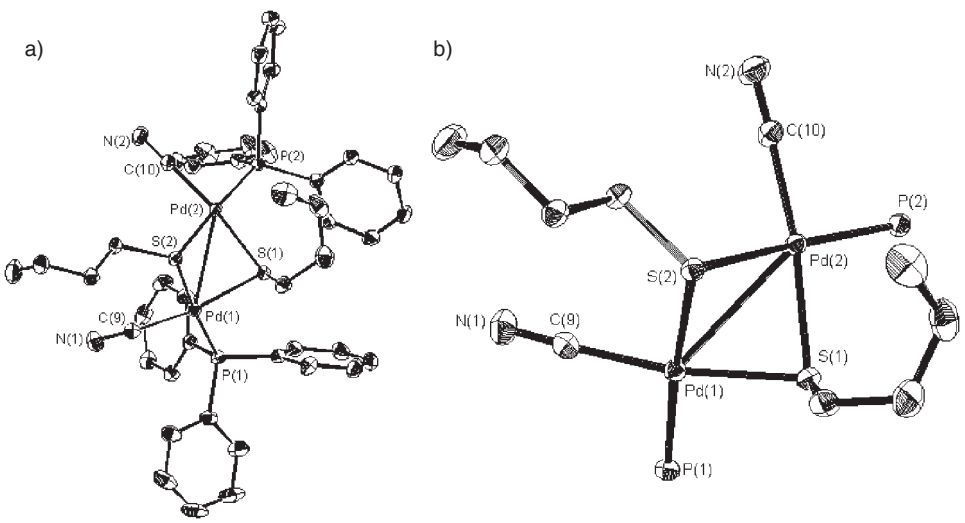
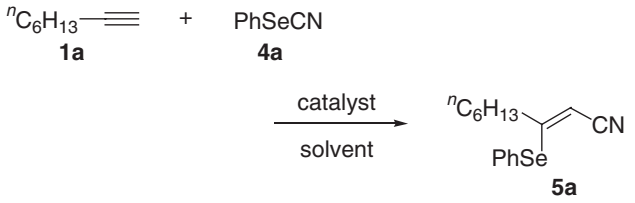


Figure 1. a) ORTEP drawing of complex **C** (50% probability thermal ellipsoids). All hydrogen atoms are omitted for clarity. b) Phenyl rings are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–Pd(2) 3.0486(2), Pd(1)–S(1) 2.3478(5), Pd(1)–S(2) 2.3489(6), Pd(1)–P(1) 2.2912(6), Pd(1)–C(9) 1.982(2), Pd(2)–S(1) 2.3544(6), Pd(2)–S(2) 2.3408(5), Pd(2)–P(2) 2.2983(5), Pd(2)–C(10) 1.983(2), Pd(2)–Pd(1)–S(1) 49.678(16), Pd(2)–Pd(1)–S(2) 49.338(14), Pd(2)–Pd(1)–P(1) 127.125(15), Pd(2)–Pd(1)–C(9) 120.58(7), S(1)–Pd(1)–S(2) 80.48(2), S(1)–Pd(1)–P(1) 95.54(2), S(1)–Pd(1)–C(9) 170.00(6), S(2)–Pd(1)–P(1) 175.91(2), S(2)–Pd(1)–C(9) 94.08(7), P(1)–Pd(1)–C(9) 89.73(7), Pd(1)–Pd(2)–S(1) 49.489(13), Pd(1)–Pd(2)–S(2) 49.568(16), Pd(1)–Pd(2)–P(2) 129.004(18), Pd(1)–Pd(2)–C(10) 122.79(6), S(1)–Pd(2)–S(2) 80.50(2), S(1)–Pd(2)–P(2) 96.85(2), S(1)–Pd(2)–C(10) 172.27(6), S(2)–Pd(2)–P(2) 177.25(2), S(2)–Pd(2)–C(10) 94.11(7), P(2)–Pd(2)–C(10) 88.60(7).

Table 6. Transition-Metal-Catalyzed Reaction of 1-Octyne with PhSeCN[a)]



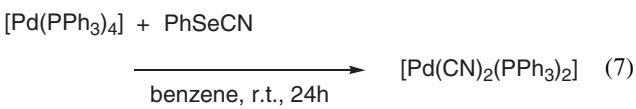
Entry	Catalyst	Solvent	Temp /°C	Time /h	Yield /%[b)]
1	$[Pd(PPh_3)_4]$	benzene	80	19	0
2	$[Pd(PPh_3)_4]$	CH_3CN	80	19	0
3	$PdCl_2$ (+Py 6 mol %)	benzene	80	20	0
4	$[RhCl(PPh_3)_3]$	CH_3CN	80	24	0
5	$[RhCl(PPh_3)_3]$	CH_3CN	120	21	0
6	$[Rh(CO)Cl(PPh_3)_3]$	CH_3CN	80	20	0

a) Reaction conditions: catalyst (3 mol %), **1a** (1.0 mmol), **4a** (1.0 mmol), solvent (1 mL). b) Determined by ^{1}H NMR.

the aromatic substituent, decreasing the coordination ability. In contrast, aliphatic group on sulfur increases the coordination ability and makes it possible to bridge both palladium ions. Bridged thio groups are probably less reactive in comparison with monodentate thio groups. Accordingly, binuclear palladium complex (complex **C**) seems less effective for the desired cyanothiolation in comparison with mononuclear complex (complex **B**).

Since the cobalt- or palladium-catalyzed cyanothiolation of alkynes with thiocyanates was observed, as shown above, it might be expected that this catalytic system is applicable to the corresponding organoselenium compounds. Therefore, we next examined the transition-metal-catalyzed addition reaction of selenocyanates to alkynes. At first, the reaction of 1-octyne with phenyl selenocyanate was examined in the presence of several transition-metal catalysts (Table 6).

When the reaction of 1-octyne with PhSeCN in the presence of 3 mol % of $[Pd(PPh_3)_4]$, which is an active catalyst for the cyanothiolation, was examined, a small amount of diphenyl diselenide was obtained, but the desired cyanoselenation did not proceed at all (Entries 1 and 2). Some other palladium and rhodium complexes such as $PdCl_2$, $[RhCl(PPh_3)_3]$, and $[Rh(CO)Cl(PPh_3)_3]$ were also ineffective (Entries 3–6).



Thus, we examined the stoichiometric reaction of PhSeCN with $[Pd(PPh_3)_4]$, which afforded not the desired $[Pd(CN)(PPh_3)_2(SePh)]$ but $[Pd(CN)_2(PPh_3)_2]$ (eq 7 and Figure 2). This is probably because the Pd–Se bond is less stable than the P–S bond, decomposing to give the diselenide and $[Pd(CN)_2(PPh_3)_2]$.

Next, we examined the $[Co_2(CO)_8]$-catalyzed reaction of 1-octyne with PhSeCN under several reaction conditions, and the results are summarized in Table 7. When the $[Co_2(CO)_8]$-catalyzed cyanoselenation was conducted under the pressure of carbon monoxide, the selenative carbonylation product was not

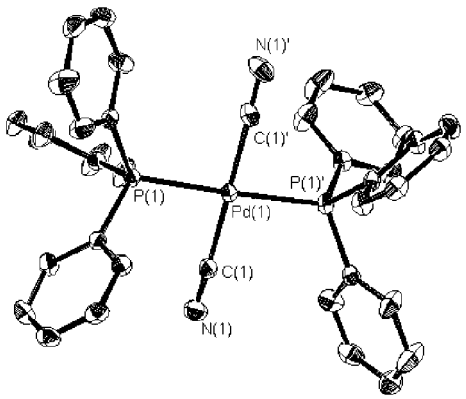
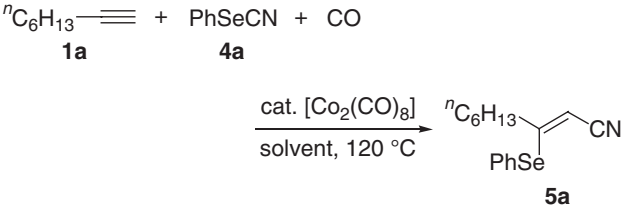


Figure 2. ORTEP drawing of $[Pd(CN)_2(PPh_3)_2]$ (50% probability thermal ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–P(1) 2.3313(7), Pd(1)–P(1)′ 2.3313(7), Pd(1)–C(1) 2.003(3), Pd(1)–C(1)′ 2.003(3), P(1)–Pd(1)–P(1)′ 174.94(2), P(1)–Pd(1)–C(1)′ 92.45(9), P(1)–Pd(1)–C(1) 87.41(9), C(1)–Pd(1)–C(1)′ 176.85(12).

Table 7. $[Co_2(CO)_8]$-Catalyzed Addition of PhSeCN to 1-Octyne in the Presence of CO[a)]



Entry	**1a** /mmol	**4a** /mmol	Solvent	Time /h	Yield /%[b)]	[*E*/*Z*]
1	1	3	CH_3CN	25	7	[0/100]
2	3	1	CH_3CN	25	12	[0/100]
3	10	1	CH_3CN	25	26	[0/100]
4	3	1	THF	16	10	[0/100]
5	3	1	benzene	16	29	[0/100]
6	10	1	benzene	18	23	[0/100]
7	3	1	CH_2Cl_2	20	38	[0/100]
8[c)]	3	1	CH_2Cl_2	22	25	[0/100]

a) Reaction conditions: $[Co_2(CO)_8]$ (3 mol %), solvent (1 mL), CO (3 MPa). b) Determined by ^{1}H NMR. c) In the absence of CO.

formed at all but the cyanoselenation product was obtained with excellent regio- and stereoselectivities, accompanied by the formation of diphenyl diselenide as a by-product. The influence of solvents on the cyanoselenation was examined. Among the solvents employed, polar solvent such as CH_3CN was ineffective (Entries 1–3) and the use of CH_2Cl_2 was most effective (Entry 7). On the other hand, the use of excess PhSeCN led to low yield (7%) (Entry 1). The reaction in the absence of carbon monoxide resulted in the decrease in yield (Entry 8). Consequently, the $[Co_2(CO)_8]$-catalyzed cyanoselenation was found to require pressurized carbon monoxide (3 MPa) and the use of excess alkyne (Entry 7).

Conclusion

In summary, the highly regio- and stereoselective [Pd-

$(PPh_3)_4$]- and $[Co_2(CO)_8]$-catalyzed cyanothiolation of terminal alkynes with thiocyanates has been disclosed. Oxidative addition of thiocyanates to the palladium(0) complex was confirmed by X-ray analysis. In addition, the $[Co_2(CO)_8]$-catalyzed cyanoselenation of terminal alkynes with selenocyanates in the pressure of carbon monoxide has been also developed.

Experimental

General. ^{1}H NMR spectra were recorded on JEOL JNM-GSX 270 (270 MHz), JEOL JNM-AL 400 (400 MHz), or Varian GEMINI 2000 (300 MHz) spectrometers using $CDCl_3$ as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra were taken on JEOL JNM-GSX-270 (68 MHz), JEOL JNM-GSX-400 (100 MHz), or Varian GEMINI 2000 (75 MHz) spectrometers using $CDCl_3$ as the solvent. ^{31}P NMR spectra were taken on JEOL-JNM-ECP 500 (202 MHz) spectrometers using $CDCl_3$ as the solvent. Chemical shifts in ^{1}H NMR were measured relative to $CDCl_3$ and converted to δ (Me_4Si) value by using δ ($CDCl_3$) = 7.26. Chemical shifts in ^{13}C NMR were measured relative to $CDCl_3$ and converted to δ (Me_4Si) value by using δ ($CDCl_3$) = 77.0. IR spectra were determined on a Perkin-Elmer Model 1600 spectrometer or JASCO FT/IR-8900 μ Fourier Transform Infrared Microsampling System. Mass spectra were obtained on JEOL JMS-DX303 in the analytical section of Osaka University. Elemental analyses were performed in the analytical section of Osaka University. Thiocyanates were prepared according to the literature.[11] Other materials including phenylselenocyanate were obtained from commercial supplies and purified by distillation or recrystallization before use. The purification of the products was carried out by MPLC (silica gel, 25–40 μm, length 310 mm, i.d. 25 mm), preparative TLC (PTLC) on Wakogel B-5F silica gel, or using recycling preparative HPLC (Japan Analytical Industry Co., Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent.

Procedure for the $[Co_2(CO)_8]$-Catalyzed Cyanothiolation of 1-Octyne with PhSCN. In a 50 mL stainless steel autoclave with a magnetic stirring bar under an argon atmosphere were placed $[Co_2(CO)_8]$ (0.1 mmol), CH_2Cl_2 (1 mL), 1-octyne (1.0 mmol), and phenyl thiocyanate (1.0 mmol). The vessel was purged three times with carbon monoxide and then charged at 3 MPa. The reaction was conducted with magnetic stirring for 11–84 h upon heating at 120–160 °C. After carbon monoxide was purged, the precipitates were filtered through Celite and concentrated in vacuo. Purification of the product was carried out by MPLC eluted with hexane:Et_2O = 4:1, or using a recycling preparative HPLC (Japan Analytical Industry Co., Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent.

(*Z*)-3-(Phenylthio)-2-nonenenitrile ((*Z*)-3a) (Table 2): Pale red-brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (t, J = 6.8 Hz, 3H), 1.14–1.25 (m, 6H), 1.39 (quint, J = 7.3 Hz, 2H), 2.15 (t, J = 7.6 Hz, 2H), 5.30 (s, 1H), 7.38–7.51 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.9, 22.3, 28.2, 28.3, 31.3, 36.2, 93.7, 116.1, 129.4, 129.5, 129.6, 134.9, 165.1; IR (NaCl): 3060, 2958, 2929, 2857, 2212 (CN), 1574, 1441, 1069, 1024, 749, 705, 692 cm^{-1}; MS (EI): m/z = 245 (M^+, 20). Anal. Calcd for $C_{15}H_{19}NS$: C, 73.42; H, 7.80; N, 5.71%. Found: C, 73.16; H, 7.94; N, 5.25%.

(*E*)-3-(Phenylthio)-2-nonenenitrile ((*E*)-3a) (Table 2): Pale red-brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, J = 6.6 Hz, 3H), 1.30–1.46 (m, 6H), 1.71 (quint, J = 7.4 Hz, 2H), 2.63 (t, J = 7.8 Hz, 2H), 4.46 (s, 1H), 7.47–7.52 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 14.0, 22.5, 28.7, 29.2, 31.4, 35.5, 89.4, 116.9, 128.6, 130.1, 130.4, 135.6, 169.4; IR (NaCl): 3057, 2956, 2929, 2858, 2210 (CN), 1579, 1476, 1466, 1441, 1068, 1024, 790, 751, 705, 691 cm^{-1}; MS (EI): m/z = 245 (M^+, 26). Anal. Calcd for $C_{15}H_{19}NS$: C, 73.42; H, 7.80; N, 5.71%. Found: C, 73.19; H, 7.80; N, 5.43%.

General Procedure for the $[Pd(PPh_3)_4]$-Catalyzed Cyanothiolation of Alkynes with Thiocyanates. Method A (the cyanothiolation in solvents): In a 50 mL stainless steel autoclave with a magnetic stirring bar under an argon atmosphere were placed $[Pd(PPh_3)_4]$ (0.1 mmol), benzene (1 mL), alkyne (1.0 mmol), and thiocyanate (1.0 mmol). The vessel was purged three times with argon and then charged at 0.1 MPa. The reaction was conducted with magnetic stirring for 66 h upon heating at 120 °C. After carbon monoxide was purged, the precipitates were filtered through Celite and concentrated in vacuo. Purification of the product was carried out by MPLC eluted with hexane/Et_2O.

Method B (the cyanothiolation in the absence of solvents): In a flame-dried two-necked flask (20 mL) with a reflux condenser and a magnetic stirring bar under a nitrogen atmosphere were placed $[Pd(PPh_3)_4]$ (0.1 mmol), alkyne (1.0 mmol), and thiocyanate (1.0 mmol). The reaction was conducted with magnetic stirring for 20–66 h upon heating at 120 °C. After the reaction was complete, the precipitates were filtered through Celite and concentrated in vacuo. Purification of the product was carried out by recycling preparative HPLC and TLC (PTLC).

(*Z*)-6-Methyl-3-(phenylthio)-2-heptenenitrile (3b) (Table 5, Entry 1): Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.72 (d, J = 6.2 Hz, 6H), 1.25–1.40 (m, 3H), 2.15 (t, J = 7.6 Hz, 2H), 5.30 (s, 1H), 7.38–7.52 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 22.0, 27.3, 34.2, 37.5, 93.3, 116.1, 129.3, 129.3, 129.6, 134.9, 165.9; IR (NaCl): 3059, 2957, 2930, 2869, 2211 (CN), 1573, 1441, 1386, 1368, 1309, 1082, 1069, 1024, 749, 706, 692 cm^{-1}; MS (EI): m/z = 231 (M^+, 8.5). Anal. Calcd for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.05%. Found: C, 72.33; H, 7.39; N, 5.99%.

(*Z*)-3-(Phenylthio)-2-heptenedinitrile (3c) (Table 5, Entry 2): Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.76 (quint, J = 7.0 Hz, 2H), 2.25 (t, J = 7.2 Hz, 2H), 2.36 (t, J = 7.3 Hz, 2H), 5.41 (s, 1H), 7.35–7.52 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 16.1, 23.8, 34.5, 95.8, 115.4, 118.4, 128.4, 129.7, 130.0, 134.6, 162.3; IR (NaCl): 3048, 2943, 2246 (CN), 2212 (CN), 1573, 1475, 1455, 1441, 1424, 1024, 751, 705, 692 cm^{-1}; MS (EI): m/z = 229 ($[M + H]^+$, 8.6). HRMS calcd for $C_{13}H_{13}N_2S$ $[M + H]^+$ 229.0799, found 229.0809.

4-Phenyl-3-(phenylthio)-2-butenenitrile [*E*/*Z*-Mixture] (3d) (Table 5, Entry 3): Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.42 (t, J = 0.75 Hz, 2H), 3.95 (s, 2H), 4.58 (s, 1H), 5.11 (t, J = 1.4 Hz, 1H), 6.93–7.49 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.2, 77.2, 77.2, 95.2, 95.3, 116.0, 127.4, 128.8, 128.9, 129.1, 129.5, 129.9, 135.4, 135.7, 164.3; IR

(NaCl): 3061, 3028, 2924, 2210 (CN), 1574, 1495, 1474, 1454, 1441, 1069, 1024, 783, 692 cm^{-1}; MS (EI): $m/z = 251$ (M^+, 23). HRMS calcd for $C_{16}H_{13}NS$ 251.0770, found 251.0768.

(*Z*)-3-(1-Cyclohexenyl)-3-(phenylthio)propenenitrile ((*Z*)-3e) (Table 5, Entry 4): Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43–1.72 (m, 4H), 2.16–2.22 (m, 2H), 2.30–2.36 (m, 2H), 4.54 (s, 1H), 6.24 (sept like, $J = 1.8$ Hz, 1H), 7.42–7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 22.2, 25.3, 27.7, 88.0, 117.4, 129.5, 130.0, 130.2, 133.0, 134.0, 135.3, 168.8; IR (NaCl): 3036, 2932, 2858, 2835, 2208 (CN), 1558, 1475, 1441, 748, 706 cm^{-1}; MS (EI): $m/z = 241$ (M^+, 36). Anal. Calcd for $C_{15}H_{15}NS$: C, 74.65; H, 6.26; N, 5.80%. Found: C, 74.70; H, 6.55; N, 5.29%. HRMS calcd for $C_{15}H_{15}NS$ 241.0927, found 241.0921.

(*E*)-3-(1-Cyclohexenyl)-3-(phenylthio)propenenitrile ((*E*)-3e) (Table 5, Entry 4): Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47–1.50 (m, 4H), 2.05–2.09 (m, 4H), 5.56 (s, 1H), 6.46 (t, $J = 4.1$ Hz, 1H), 7.27–7.32 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 22.1, 26.0, 26.9, 96.7, 116.9, 127.8, 129.1, 131.3, 133.2, 134.6, 136.5, 161.4; IR (NaCl): 3048, 2932, 2860, 2361, 2210 (CN), 1555, 1479, 1458, 745, 689 cm^{-1}; MS (EI): $m/z = 241$ (M^+, 110). HRMS calcd for $C_{15}H_{15}NS$ 241.0927, found 241.0921.

(*Z*)-3-Phenyl-3-(phenylthio)propenenitrile (3f) (Table 5, Entry 5): Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.65 (s, 1H), 7.16–7.44 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.2, 97.2, 128.3, 128.5, 128.6, 129.1, 130.6, 131.4, 132.6, 136.3, 161.6; IR (NaCl): 2924, 2854, 2210 (CN), 1556, 1441, 745, 691 cm^{-1}; MS (EI): $m/z = 237$ (M^+, 22). HRMS calcd for $C_{15}H_{11}NS$ 237.0613, found 237.0609.

3-(4-Methylphenyl)-3-(phenylthio)propenenitrile [*E*/*Z*-Mixture] (3g) (Table 5, Entry 6): Deep yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.40 (s, 3H), 4.70 (s, 1H), 5.64 (s, 1H), 7.05–7.59 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2, 21.3, 89.1, 96.7, 116.6, 117.6, 128.2, 128.4, 129.1, 129.4, 129.6, 130.3, 130.6, 131.7, 132.3, 133.4, 135.4, 141.2, 141.3, 161.2, 166.2; IR (NaCl): 3055, 3020, 2918, 2156 (CN), 1578, 1475, 1439, 810, 737, 687 cm^{-1}; MS (EI): $m/z = 251$ (M^+, 13). HRMS calcd for $C_{16}H_{13}NS$ 251.0770, found 251.0767.

General Procedure for the Transition-Metal-Catalyzed Cyanoselenation of 1-Octyne with Selenocyanates. Method A: In a flame-dried two-necked flask (20 mL) with a reflux condenser and a magnetic stirring bar under a nitrogen atmosphere were placed catalyst (0.03 mmol), 1-octyne (1.0 mmol), and phenyl selenocyanate (1.0 mmol). The reaction was conducted with magnetic stirring for 19–24 h upon heating at 80 °C. After the reaction was complete, the precipitates were filtered through Celite and concentrated in vacuo. Purification of the product was carried out by MPLC eluted with hexane:Et_2O = 7:3.

Method B: In a 50 mL stainless steel autoclave with a magnetic stirring bar under an argon atmosphere were placed [$Co_2(CO)_8$] (3 mol %), solvent (1 mL), 1-octyne (1.0–10 mmol), and selenocyanate (1.0–3.0 mmol). The vessel was purged three times with carbon monoxide and then charged at 3 MPa. The reaction was conducted with magnetic stirring for 20 h upon heating at 120 °C. After carbon monoxide was purged, precipitates were filtered through Celite and concentrated in vacuo. Purification of the product was carried out by MPLC eluted with hexane:Et_2O = 7:3.

(*Z*)-3-(Phenylseleno)-2-nonenenitrile (5a) (Table 6): Pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.83 (t, $J = 6.8$ Hz, 3H), 1.11–1.38 (m, 8H), 2.18 (t, $J = 7.3$ Hz, 2H), 5.60 (s, 1H), 7.33–7.63 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.9, 22.4, 28.2, 28.5, 31.2, 37.9, 96.7, 116.6, 129.4, 130.4, 132.7, 136.4, 165.0; IR (NaCl): 3069, 2966, 2958, 2931, 2862, 2276 (CN), 1569, 1483, 1353, 741, 690 cm^{-1}.

Procedure for the Synthesis of [Pd(CN)(PPh_3)$_2$(SPh)]. In a two-necked flask (20 mL) equipped with a magnetic stirring bar under a nitrogen atmosphere were placed [$Pd(PPh_3)_4$] (350 mg, 0.25 mmol), benzene (1 mL), and PhSCN (280 mg, 0.25 mmol). The mixture was stirred for 24 h at room temperature. The precipitate was filtered and washed with benzene to give yellow solid. Recrystallization from $C_2H_4Cl_2$/benzene afforded pure *trans*-[Pd(CN)(PPh_3)$_2$(SPh)] (79% yield). Red solid; mp 229–230 °C; ^{31}P NMR (202 MHz, $CDCl_3$): δ 26.22; IR (KBr): 2130 (CN) cm^{-1}; Anal. Calcd for $C_{43}H_{35}NP_2PdS$: C, 67.41; H, 4.60; N, 1.83%. Found: C, 68.19; H, 4.66; N, 1.97%.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number: CCDC-800559 for Figure 1, CCDC-800562 for Figure 2. Copies of data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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13 When the isolated (*Z*)-**3a** ($E/Z = 4/96$) was heated at

150 °C for 84 h in the presence of $[Co_2(CO)_8]$ catalyst, *Z* to *E* isomerization took place to give **3a** with the *E*/*Z* ratio of 82/18. Similarly, upon heating the isolated (*Z*)-**3a** (*E*/*Z* = 4/96) at 130 °C for 66 h in the presence of $[Pd(PPh_3)_4]$ (10 mol %) in benzene, *Z* to *E* isomerization occurred to give **3a** with the *E*/*Z* ratio of 59/41.

14 In this reaction, the starting materials were consumed, and some by-products were also obtained, e.g., the $(PhS)_2$ adduct to 1-octyne.

15 Since complex **B** is *trans*-isomer, *trans* to *cis* isomerization is required for reductive elimination of the product. Beletskaya and Ananikov suggested the *trans* to *cis* isomerization of *trans*-$[PtH(SePh)(PPh_3)_2]$ for hydroselenation of alkynes: See, Ref. 4m.

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