Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 3521–3526

TETRAHEDRON

Platinum-catalyzed highly selective thiocarbonylation of acetylenes with thiols and carbon monoxide

Jun-ichi Kawakami,[a] Masanori Mihara,[b] Ikuyo Kamiya,[c] Mitsuhiro Takeba,[b] Akiya Ogawa[c,*] and Noboru Sonoda[d]

[a]*Chemical Development Laboratories, Takeda Chemical Industries, Ltd., 2-17-85 Jusohonmachi, Yodogawa-ku, Osaka 532-8686, Japan*
[b]*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*
[c]*Department of Chemistry, Faculty of Science, Nara Women's University, Kitauoyanishi-machi, Nara 630-8506, Japan*
[d]*Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564-0073, Japan*

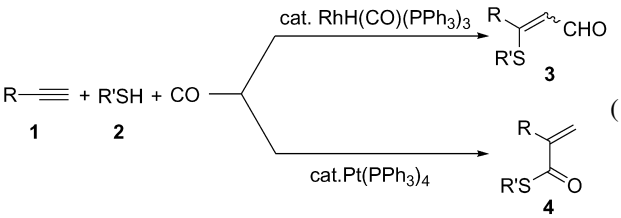
Received 8 January 2003; accepted 19 March 2003

Abstract—A novel carbonylative addition of thiols (RSH) to terminal acetylenes (R′–C≡CH) takes place successfully in the presence of platinum catalysts under the pressure of carbon monoxide, providing α,β-unsaturated thioesters (R′–C(C(O)SR)=CH_2) in good yields regioselectively. This 'hydrothiocarbonylation' reaction of acetylenes may include the formation of the platinum sulfide complex as key species. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Although the transition-metal-catalyzed reactions of organic silicon,[1] tin,[2] and boron[3] compounds have been established for effecting a wide range of synthetic reactions, the use of organosulfur compounds in transition-metal-catalyzed reactions has been largely unexplored.[4] Most probably, the widespread prejudice that 'sulfur compounds are catalyst poisons' has precluded investigation in this area. Very recently, however, transition-metal-catalyzed highly selective methods for the introduction of sulfur-containing groups into carbon–carbon unsaturated bonds have been reported,[5] i.e. bisthiolation,[6–8] hydrothiolation,[9] thioboration,[10] thiosilylation,[11] thiophosphorylation,[12] thioesterification,[13] *S*-propargylation or allylation of thiols,[14] and carbothiolation,[15] etc.[16] With regard to the transition-metal-catalyzed reaction of thiols with carbon monoxide, the $Co_2(CO)_8$-catalyzed desulfurizative carbonylation of thiols was reported as a series of pioneering work.[17] The $Co_2(CO)_8$-catalyzed carbonylation of organic diselenide or ditelluride has also been developed to give the corresponding seleno and telluro ethers, respectively.[18]

Recently, we have discovered the first example of $RhH(CO)(PPh_3)_3$-catalyzed 'thioformylation' of acetylenes with thiols and carbon monoxide (Eq. (1)).[19] This thioformylation exhibits the excellent regioselectivity where carbon monoxide and a thio group are introduced selectively into the terminal and inner positions of acetylenes, respectively. Furthermore, we have disclosed that switching the catalyst simply from $RhH(CO)(PPh_3)_3$ to $Pt(PPh_3)_4$ leads to a sharp reversal of regioselectivity of CO introduction ('hydrothiocarbonylation') (Eq. (1)).[20]



(1)

In this paper, we describe full details of this platinum-catalyzed carbonylative addition of thiols to acetylenes under the pressure of carbon monoxide. This platinum-catalyzed reaction provides a general method for the regioselective synthesis of α,β-unsaturated thioesters.

2. Results and discussion

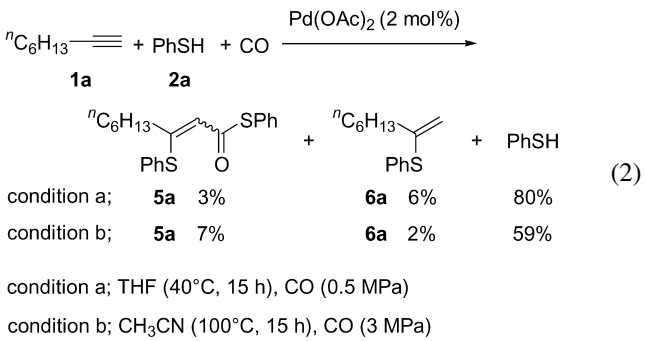
2.1. Screening of Group 10 transition-metal-catalyzed reaction of 1-octyne with benzenethiol and carbon monoxide

Our recent investigations have proved that transition metal complexes such as Pd, Pt and Rh complexes are effective catalysts for regioselective hydrothiolation of carbon–carbon unsaturated compounds with thiols.[9a,c,d] Therefore,

Keywords: thiocarbonylation; platinum; thiols; carbon monoxide; acetylenes.
* Corresponding author; e-mail: a.ogawa@cc.nara-wu.ac.jp

0040–4020/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0040-4020(03)00485-X

it might be expected that these complexes exhibit catalytic activities toward the desired carbonylative addition of thiols to acetylenes in the presence of carbon monoxide. At first, we started the carbonylative addition by using $Pd(OAc)_2$, which is a useful catalyst for the addition of thiols to acetylenes. However, the attempted reaction provided only small amounts of the carbonylative addition product **5a**[21] and the thiol addition product **6a** with the recovery of 80% of the starting thiol (Eq. (2), condition a). This result clearly indicates the pressurized carbon monoxide retarded the catalytic activity of $Pd(OAc)_2$ even for the simple addition reaction.

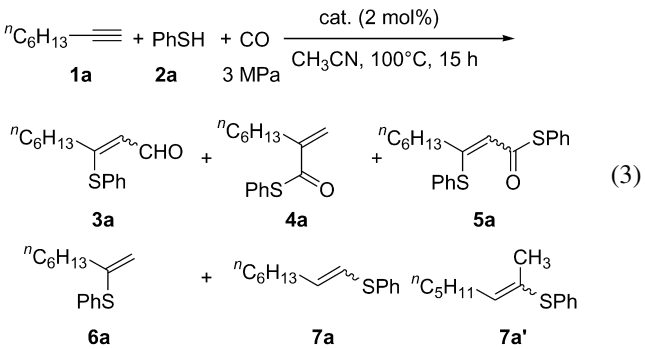


(2)

condition a; THF (40°C, 15 h), CO (0.5 MPa)

condition b; CH_3CN (100°C, 15 h), CO (3 MPa)

A similar reaction in acetonitrile led to the increase in the yield of the product **5a** slightly (Eq. (2), condition b). Next we examined the reaction of benzenethiol with 1-octyne and carbon monoxide under similar conditions by employing some other Group 10 transition metal catalysts, and the results are shown in Table 1 (Eq. (3)).



(3)

$Pd(PPh_3)_4$ is an excellent catalyst for both the stereoselective addition of diaryl disulfides to terminal acetylenes and the carbonylative addition of diaryl disulfides to terminal acetylenes under the pressure of carbon monoxide.[6] However, the attempted reaction of benzenethiol with 1-octyne and carbon monoxide in the presence of $Pd(PPh_3)_4$ provided carbonylation products **4a** and **5a** in 4 and 13% yields, respectively (entry 2). Palladium complexes such as $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$ and $Pd_2(dba)_3$ resulted in the formation of a complex mixture (entries 3–5). As the result, palladium complexes examined did not exhibit high catalytic activity for the desired carbonylative addition.[22] Interestingly, platinum complex like $Pt(PPh_3)_4$ exhibited relatively high catalytic activity toward the desired carbonylation giving **4a** in 32% yield (entry 6). The reaction in the presence of $NiCl_2(PPh_3)_2$ or in the absence of catalyst did not afford the carbonylation products (entries 7 and 8).

Table 1. Group 10 transition-metal-catalyzed reaction of 1-octyne with benzenethiol and carbon monoxide

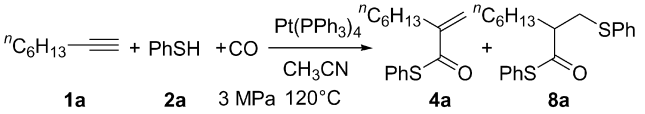
Entry	Catalyst	Yield (%)[a]				
		3a	**4a**	**5a**	**6a**	**7a+7a'**
1	$Pd(OAc)_2$	0	0	7	2	20
2	$Pd(PPh_3)_4$	0	4	13	6	0
3	$PdCl_2(PPh_3)_2$	0	13	19	0	0
4	$PdCl_2(PhCN)_2$	0	0	7	1	8
5	$Pd_2(dba)_3$	0	0	5	Trace	0
6	$Pt(PPh_3)_4$	0	32	7	Trace	0
7	$NiCl_2(PPh_3)_2$	0	Trace	Trace	0	0
8	None	0	0	0	0	0

Reaction condition. **1a** (1 mmol), **2a** (1 mmol), CO (3 MPa), catalyst (2 mol%), CH_3CN (1 mL), 100°C, 15 h.

[a] Determined by ^1H NMR.

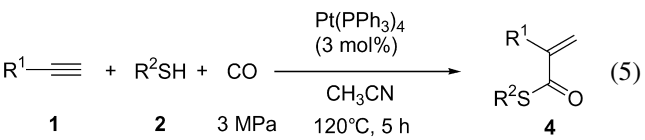
2.2. $Pt(PPh_3)_4$-Catalyzed hydrothiocarbonylation of acetylenes with thiols and carbon monoxide

As mentioned above (entry 6 in Table 1), the $Pt(PPh_3)_4$-catalyzed reaction of 1-octyne (**1a**) with benzenethiol (**2a**) and carbon monoxide provided **4a** in 32% yield. We optimized this $Pt(PPh_3)_4$-catalyzed reaction by examining the reactions conducted under various reaction conditions (Eq. (4), Table 2).



(4)

When the reaction of 1-octyne (1.5 equiv.) was carried out under 3 MPa of carbon monoxide at 120°C for 15 h, the yield of the α,β-unsaturated thioester (**4a**) was increased to 60% (entry 1). The hydrothiocarbonylation product (**4a**), which has an α,β-unsaturated carbonyl unit, is subjected to conjugate addition of benzenethiol to give **8a** in 14% yield concomitantly (entry 1). However, the use of excess 1-octyne (5.5 equiv.) in this reaction afforded **4a** in 83% yield exclusively (entry 3). On the other hand, the reaction employing excess benzenethiol (2 equiv.) provided **8a** predominantly (entry 4).



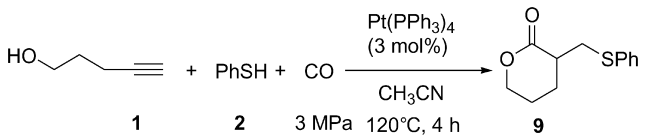
(5)

Table 2. $Pt(PPh_3)_4$-Catalyzed reaction of 1-octyne with benzenethiol and carbon monoxide

Entry	Molar ratio of **1a/2a**	Time (h)	Yield (%)[a]	
			4a	**8a**
1	1.5	15	60	14
2	3.5	15	71	6
3	5.5	1	83	–
4	0.5	15	–	77

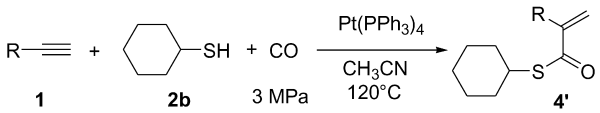
Reaction condition. **1a** (2.5–27.5 mmol), **2a** (5 mmol), CO (3 MPa), $Pt(PPh_3)_4$ (3 mol%), CH_3CN (5 mL), 120°C.

[a] Based on **2a** employed.



(6)

Table 3 lists the results of the $Pt(PPh_3)_4$-catalyzed hydrothiocarbonylation using some thiols and acetylenes (Eq. (5)). The hydrothiocarbonylation with aromatic thiols such as *p*-methoxybenzenethiol took place regioselectively to provide the α,β-unsaturated thioesters in good yields (entry 2). In the case of aliphatic thiols, the same hydrothiocarbonylation also proceeded smoothly with excellent regioselectivity (entries 3 and 4). Similar conditions can be employed with aliphatic acetylenes (entries 5–7). Noteworthy is that $Pt(PPh_3)_4$ exhibits an excellent catalytic activity for the regioselective hydrothiocarbonylation with aliphatic thiols, being different from the Rh-catalyzed thioformylation, which takes place only in the case using aromatic thiols.[19] When the carbonylation of 5-hydroxy-1-pentyne was carried out in the presence of benzenethiol (1 equiv.) and $Pt(PPh_3)_4$ (3 mol%) under 3 MPa of carbon monoxide at 120°C for 4 h, the cyclocarbonylation of 5-hydroxy-1-pentyne took place successfully to give α-[(phenylthio)methyl]-δ-lactone (**9**) selectively in 73% yield (Eq. (6)).[23]



(7)

We next investigated the $Pt(PPh_3)_4$-catalyzed hydrothiocarbonylation of aliphatic thiol such as cyclohexanethiol (**2b**) in further details (Eq. (7), Table 4). In the case of benzenethiol, the use of excess acetylenes is essential to depress the further addition reaction of benzenethiol to the α,β-unsaturated thioesters, while the hydrothiocarbonylation with aliphatic thiols, which are less acidic than aromatic ones, proceeds smoothly by the use of equimolar amount of acetylene to give the α,β-unsaturated thioesters regioselectively in excellent yield (entry 2). Even in the case using excess amounts of thiols, the α,β-unsaturated thioester (**4d**) was obtained selectively in good yield (entry 3).

Entries 4–6 in Table 4 show the results of the $Pt(PPh_3)_4$-catalyzed hydrothiocarbonylation of cyclohexylthiol with several terminal acetylenes. The hydrothiocarbonylation of aromatic acetylenes also took place regioselectively (entry 6).

Table 3. $Pt(PPh_3)_4$-Catalyzed hydrothiocarbonylation of acetylenes with thiols and carbon monoxide

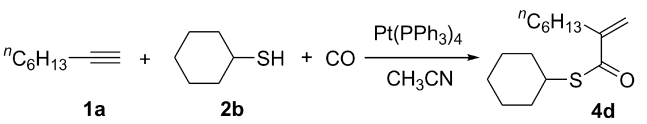
Entry	Alkyne **1**, R^1	Thiol **2**, R^2	Product **4**	Isolated yield (%)[a]
1	$^nC_6H_{13}$	Ph	**4a**	83
2		*p*-MeO–C_6H_4	**4b**	86
3		$^nC_8H_{17}$	**4c**	87
4		$^cC_6H_{11}$	**4d**	94
5	$(CH_3)_2CH(CH_2)_2$	Ph	**4e**	70
6	$PhCH_2$		**4f**	63
7	$NC(CH_2)_3$		**4g**	75

Reaction condition. **1** (37.5 mmol), **2a** (5 mmol), CO (3 MPa), $Pt(PPh_3)_4$ (3 mol%), CH_3CN (5 mL), 120°C, 1–7 h.
[a] Based on thiols employed.

Table 4. $Pt(PPh_3)_4$-Catalyzed hydrothiocarbonylation of acetylenes with cyclohexanethiol and carbon monoxide

Entry	Alkyne **1**, R	Molar ratio of **1**/**2b**	Product **4'**	Isolated yield (%)[a]
1	$^nC_6H_{13}$	7.5	**4d**	94
2		1.0	**4d**	99
3		0.5	**4d**	99[b]
4	$(CH_3)_2CH(CH_2)_2$	1.0	**4h**	87
5	$NC(CH_2)_3$	1.0	**4i**	82
6	Ph	1.0	**4j**	62

Reaction condition. **1** (5–37.5 mmol), **2b** (5–10 mmol), CO (3 MPa), $Pt(PPh_3)_4$ (3 mol%), CH_3CN (5 mL), 120°C, 1–7 h.
[a] Based on cyclohexanethiol employed.
[b] Based on acetylene employed.

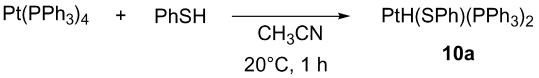


(8)

As mentioned above, hydrothiocarbonylation product **4d** can be obtained in high yield, when the $Pt(PPh_3)_4$-catalyzed reaction was carried out using 1-octyne (1 equiv.) under 3 MPa of carbon monoxide at 120°C (Eq. (8), Table 5, entry 1). Lower temperature (80°C) only gave **4d** in 24% yield and recovered cyclohexylthiol (entry 2). Under 0.5 MPa of carbon monoxide, the carbonylation proceeds smoothly (entry 3).

2.3. A possible reaction pathway for $Pt(PPh_3)_4$-catalyzed hydrothiocarbonylation of acetylenes with thiols and carbon monoxide

To explore the reaction pathway for the $Pt(PPh_3)_4$-catalyzed hydrothiocarbonylation, stoichiometric reaction of the platinum catalyst with benzenethiol was examined. The equimolar reaction of $Pt(PPh_3)_4$ with PhSH at 20°C in acetonitrile under argon atmosphere afforded a yellow solid **10a** (Eq. (9)). ^1H NMR spectra indicated the appearance of the signal at δ −10.01. This result and the melting point of the yellow solid suggest the formation of *trans*-$PtH(SPh)(PPh_3)_2$ (**10a**) reported in the literature.[24] The reaction of benzenethiol with 1-octyne (**1a**) in the presence of complex **10a** as a catalyst afforded the corresponding product **4a** in good yield (Eq. (10)).

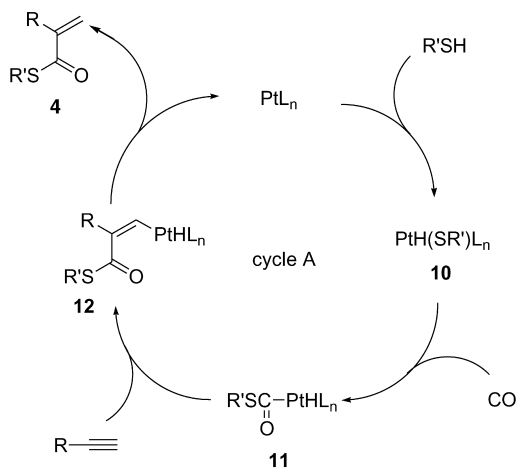


(9)

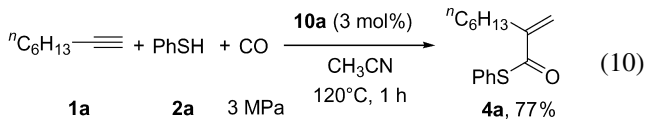
Table 5. $Pt(PPh_3)_4$-Catalyzed hydrothiocarbonylation of 1-octyne with cyclohexanethiol and carbon monoxide

Entry	CO (MPa)	Temperature (°C)	Product **4d**, Yield (%)[a]
1	3	120	99
2	3	80	24
3	0.5	120	85

Reaction condition. **1** (5 mmol), **2b** (5 mmol), CO (0.5–3 MPa), $Pt(PPh_3)_4$ (3 mol%), CH_3CN (5 mL), 80–120°C, 2 h.
[a] Based on cyclohexanethiol employed.



Scheme 1.



(10)

Although elucidation of the precise mechanism requires further detailed investigation, the catalytic cycle A for hydrothiocarbonylation is proposed as a possible reaction path (Scheme 1).[25] The oxidative addition of R′SH to PtL_n affords $PtH(SR')L_n$ (**10**). The insertion of CO into the Pt–S bond of **10** leads to **11**. The insertion of acetylene into Pt–C bond of **11** forms the vinylplatinum complex (**12**), and the subsequent reductive elimination with the regeneration of PtL_n provides the hydrothiocarbonylation product **4**.

3. Conclusion

We have developed the platinum-catalyzed highly selective hydrothiocarbonylation of acetylenes with thiols and carbon monoxide. α,β-Unsaturated thioesters can be produced in good yields in the presence of catalytic amounts of $Pt(PPh_3)_4$. This reaction provides a general method for the regioselective introduction of thiols and carbon monoxide to acetylenes.

4. Experimental

4.1. General procedure for the $Pt(PPh_3)_4$-catalyzed hydrothiocarbonylation of acetylenes with carbon monoxide and aromatic thiols

In a 50 mL stainless steel autoclave with a magnetic stirring bar under argon atmosphere were placed $Pt(PPh_3)_4$ (3 mol%), acetonitrile (5 mL), acetylene (37.5 mmol), and aromatic thiol (5 mmol). Carbon monoxide was purged for three times and then charged at 3 MPa. The reaction was conducted with magnetic stirring for 2 h upon heating at 120°C. After carbon monoxide was purged, the resulting mixture was filtered through Celite and concentrated in vacuo. Purification of the product was carried out by MPLC (silica gel, 25–40 μm, length 310 mm, i.d. 25 mm, eluent *n*-hexane–Et_2O=4:1).

4.1.1. 2-(Phenylthiocarbonyl)-1-octene (4a). A colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.20–1.40 (m, 6H), 1.48 (quint, *J*=6.8 Hz, 2H), 2.34 (t, *J*=7.3 Hz, 2H), 5.65 (s, 1H), 6.21 (s, 1H), 7.35–7.50 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.5, 28.2, 28.8, 31.5, 32.0, 122.7, 127.8, 129.1, 129.3, 134.9, 148.4, 191.7; IR (NaCl) 3070, 2927, 2856, 1680, 1478, 1440, 965, 745, 688 cm^{-1}; MS (EI), *m*/*z*=248 (M^+, 13.6). Anal. calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12; S, 12.91. Found: C, 72.34; H, 8.17; S, 12.82.

4.1.2. 2-(*p*-Methoxyphenylthiocarbonyl)-1-octene (4b). A colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.20–1.40 (br s, 6H), 1.48 (quint, *J*=6.8 Hz, 2H), 2.34 (t, *J*=7.6 Hz, 2H), 3.82 (s, 3H), 5.64 (s, 1H), 6.20 (s, 1H), 6.94 (d, *J*=8.8 Hz, 2H), 7.33 (d, *J*=8.8 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.5, 28.2, 28.9, 31.5, 32.0, 55.3, 114.8, 18.5, 122.5, 136.4, 148.4, 160.6, 192.7; IR (NaCl) 3090, 2928, 2857, 1678, 1626, 1594, 1495, 1463, 1291, 1250, 1174, 1033, 966, 826 cm^{-1}; MS (EI), *m*/*z*=278 (M^+, 43.5). Anal. calcd for $C_{16}H_{22}OS$: C, 69.02; H, 7.97. Found: C, 69.26; H, 8.08.

4.1.3. 2-(Phenylthiocarbonyl)-5-methyl-1-hexene (4e). A pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (d, *J*=6.6 Hz, 6H), 1.37 (q, *J*=7.6 Hz, 2H), 1.58 (m, 1H), 2.35 (t, *J*=7.8 Hz, 2H), 5.68 (t, *J*=7.8 Hz, 2H), 5.68 (s, 1H), 6.22 (s, 1H), 7.40–7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 27.4, 29.6, 37.0, 122.6, 127.6, 129.0, 129.2, 134.8, 148.5, 191.8; IR (NaCl) 2928, 2868, 1681, 1626, 1468, 1439, 910, 745, 689 cm^{-1}; MS (EI), *m*/*z*=234 (M^+, 17.2); HRMS calcd for $C_{14}H_{18}OS$ 234.1078, found 234.1080.

4.1.4. 2-(Phenylthiocarbonyl)allylbenzene (4f). A brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.67 (s, 2H), 5.57 (s, 1H), 6.33 (s, 1H), 7.18–7.40 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 37.8, 124.6, 126.5, 127.5, 128.5, 129.1, 129.3, 134.9, 138.0, 147.6, 191.2; IR (NaCl) 3061, 3027, 1676, 1626, 1495, 1478, 1440, 973, 747, 705 cm^{-1}; MS (EI), *m*/*z*=256 (M^+, 7.1). Anal. calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55. Found: C, 75.76; H, 5.63.

4.1.5. 2-(Phenylthiocarbonyl)-5-cyano-1-pentene (4g). A pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.87 (quint, *J*=7.3 Hz, 2H), 2.35 (t, *J*=7.1 Hz, 2H), 2.51 (t, *J*=7.6 Hz, 2H), 5.81 (s, 1H), 6.34 (s, 1H), 7.42 (s, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.5, 24.0, 31.1, 119.1, 124.9, 127.1, 129.2, 129.5, 134.9, 145.8, 191.3; IR (NaCl) 3061, 2939, 2246, 1674, 1628, 1478, 1440, 970, 748, 690 cm^{-1}; MS (EI), *m*/*z*=231 (M^+, 5.2). Anal. calcd for $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; N, 6.06; S, 13.86. Found: C, 67.27; H, 5.73; N, 6.05; S, 13.49.

4.2. General procedure for the $Pt(PPh_3)_4$-catalyzed hydrothiocarbonylation of acetylenes with carbon monoxide and aliphatic thiols

In a 50 mL stainless steel autoclave with a magnetic stirring bar under argon atmosphere were placed $Pt(PPh_3)_4$ (3 mol%), acetonitrile (5 mL), acetylene (5 mmol), and

aliphatic thiol (5 mmol). Carbon monoxide was purged for three times and then charged at 3 MPa. The reaction was conducted with magnetic stirring for 2 h upon heating at 120°C. After carbon monoxide was purged, the resulting mixture was filtered through Celite and concentrated in vacuo. Purification of the product was carried out by MPLC (silica gel, 25–40 μm, length 310 mm, i.d. 25 mm, eluent *n*-hexane–Et_2O=4:1).

4.2.1. 2-(*n*-Octylthiocarbonyl)-1-octene (4c). A colorless liquid; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J=6.8 Hz, 6H), 1.20–1.50 (m, 18H), 1.59 (quint, J=7.3 Hz, 2H), 2.33 (t, J=7.6 Hz, 2H), 5.51 (s, 1H), 6.05 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.5, 22.6, 28.2, 28.85, 28.88, 29.08, 29.13, 29.5, 31.6, 31.8, 121.4, 148.8, 194.0; IR (NaCl) 2927, 2856, 1666, 1627, 1458, 974, 928 cm^{-1}; MS (EI), m/z=284 (M^+, 5.3). Anal. calcd for $C_{17}H_{32}OS$: C, 71.77; H, 11.34. Found: C, 71.63; H, 11.32.

4.2.2. 2-(*c*-Hexylthiocarbonyl)-1-octene (4d). A colorless liquid; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J=6.8 Hz, 3H), 1.20–1.36 (m, 6H), 1.37–1.54 (m, 6H), 1.62 (m, 2H), 1.72 (br quint, 2H), 1.94 (br quint, 2H), 2.31 (t, J=7.6 Hz, 2H), 3.53 (m, 1H), 5.49 (s, 1H), 6.03 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.5, 25.6, 26.0, 28.2, 28.9, 31.6, 31.8, 33.1, 42.3, 121.3, 149.0, 193.7; IR (NaCl) 2929, 2854, 2360, 1662, 1626, 1449, 1378, 1342, 1264, 1208, 1103, 996, 973, 928, 888, 818, 725, 654 cm^{-1}; MS (EI), m/z=254 (M^+, 18.5); HRMS calcd for $C_{15}H_{26}OS$ 254.1704, found 254.1705.

4.2.3. 2-(*c*-Hexylthiocarbonyl)-5-methyl-1-hexene (4h). A colorless liquid; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, J=6.8 Hz, 6H), 1.29–1.72 (m, 11H), 1.94 (m, 2H), 2.32 (t, J=8.1 Hz, 2H), 3.53 (m, 1H), 5.50 (s, 1H), 6.03 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.4, 25.6, 26.0, 27.8, 29.7, 33.1, 37.4, 42.3, 121.3, 149.2, 193.8; IR (NaCl) 2931, 2854, 1661, 1627, 1468, 1449, 1385, 1367, 1342, 1265, 1225, 1204, 1106, 984, 919, 888, 818, 653 cm^{-1}; MS (EI), m/z=240 (M^+, 3.0). Anal. calcd for $C_{14}H_{24}OS$: C, 69.95; H, 10.06. Found: C, 70.02; H, 10.18.

4.2.4. 2-(*c*-Hexylthiocarbonyl)-5-cyano-1-pentene (4i). A pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.30–1.72 (m, 8H), 1.85 (quint, J=7.3 Hz, 2H), 1.94 (m, 2H), 2.35 (t, J=7.1 Hz, 2H), 2.48 (t, J=7.3 Hz, 2H), 3.54 (m, 1H), 5.63 (s, 1H), 6.15 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.5, 24.0, 25.5, 25.9, 30.8, 33.0, 42.5, 119.2, 123.5, 146.3, 193.1; IR (NaCl) 2932, 2854, 2363, 2246, 1657, 1627, 1449, 1343, 1264, 1208, 1056, 997, 975, 933, 888, 871, 818, 757 cm^{-1}; MS (EI), m/z=237 (M^+, 2.1). Anal. calcd for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; N, 5.90. Found: C, 66.14; H, 8.28; N, 5.94.

4.2.5. 2-(*c*-Hexylthiocarbonyl)styrene (4j). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.29–1.72 (m, 8H), 1.97 (quint like, 2H), 3.60 (m, 1H), 5.75 (s, 1H), 6.15 (s, 1H), 7.33–7.37 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.6, 26.0, 32.9, 42.9, 122.3, 128.2, 128.3, 128.5, 136.2, 148.6, 193.5; IR (NaCl) 2930, 2853, 1662, 1612, 1494, 1447, 1295, 1265, 1118, 1004, 995, 972, 935, 787, 774, 698, 666 cm^{-1}; MS (EI), m/z=246 (M^+, 13.4); HRMS calcd for $C_{15}H_{18}OS$ 246.1078, found 246.1067.

Acknowledgements

This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (A) 'Exploitation of Multi-Element Cyclic Molecules' from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1. (a) Ojima, I. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, p 1687 part 2. (b) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley: Chichester, 1995; pp 488–497. (c) Hiyama, T.; Kusumoto, T. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 8, p 763. (d) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; p 1479 part 2. (e) Hiyama, T.; Shirakawa, E. *Top. Curr. Chem.* **2002**, *219*, 60. (f) Recatto, C. A. *Aldrichim. Acta* **1995**, *28*, 85. (g) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. (h) Murai, S.; Chatani, N. *J. Synth. Org. Chem. Jpn* **1993**, *51*, 421. (i) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263.
2. (a) William, J. S. *The Stille Reaction*; Wiley: New York, 1998. (b) Davies, A. G. *Organotin Chemistry*; VCH: Weinheim, 1997. (c) Fugami, K.; Kosugi, M. *Top. Curr. Chem.* **2002**, *219*, 87. (d) William, J. S. *Org. React.* **1997**, *50*, 1. (e) Harrison, P. G. *Chemistry of Tin*; Blackie: New York, 1989. (f) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. (g) Mitchell, T. N. *Synthesis* **1992**, 803. (h) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
3. (a) Miyaura, N. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; Wiley-VCH: Weinheim, 2001; pp 1–45. (b) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11. (c) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957. (d) Suzuki, A.; Miyaura, N. *J. Synth. Org. Chem. Jpn* **1993**, *51*, 1043. (e) Burgess, K.; Ohlmeyer, M. *J. Chem. Rev.* **1991**, *91*, 1179.
4. (a) Roberto, A. S.-D. *Organometallic Modeling of the Hydrosulfurization and Hydrodenitrogenation Reaction*; Kluwer Academic: Dordrecht, 2002. (b) Weber, T.; Prins, R.; van Santen, A. *Transition Metal Sulphides Chemistry and Catalysis*; Kluwer Academic: Dordrecht, 1997. (c) Stiefel, E. I.; Matsumoto, K. *Transition Metal Sulfur Chemistry Biological and Industrial Significance*; American Chemical Society: Washington, DC, 1996.
5. (a) Ogawa, A. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: New york, 2002; p 2841 Chapter VII.6. (b) El Ali, B.; Alper, H. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: New york, 2002; p 2333 Chapter VI.6. (c) Kuniyasu, H.; Kurosawa, H. *Chem. Eur. J.* **2002**, *8*, 2660. (d) Ogawa, A.; Hirao, T. *Science of Synthesis*; Lautens, M., Trost, B. M., Eds.; Georg Thieme: Stuttgart, 2001; Vol. 1, p 389. (e) Takacs, J. M.; Vayalakkada, S.; Jiang, X. *Science of Synthesis*; Lautens, M., Trost, B. M., Eds.; Georg Thieme: Stuttgart, 2001; Vol. 1, p 265. (f) Takacs, J. M.; Jiang, X.; Vayalakkada, S. *Science of Synthesis*; Lautens, M., Trost, B. M., Eds.; Georg Thieme: Stuttgart, 2001; Vol. 1, p 63.

(g) Lautens, M. *Science of Synthesis*; Lautens, M., Trost, B. M., Eds.; Georg Thieme: Stuttgart, 2001; Vol. 1, p 1. (h) Kondo, T. *J. Synth. Org. Chem. Jpn* **2001**, *59*, 170. (i) Ogawa, A. *J. Organomet. Chem.* **2000**, *611*, 463. (j) Kuniyasu, H. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; Wiley-VCH: Weinheim, 2001; p 217. (k) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205. (l) Han, L.-B.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1999**, 395. (m) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435. (n) Ogawa, A.; Sonoda, N. *J. Synth. Org. Chem. Jpn* **1996**, *894*. (o) Ogawa, A.; Sonoda, N. *J. Synth. Org. Chem. Jpn* **1993**, *51*, 815.

6. Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.
7. Kondo, T.; Uenoyama, S.; Fujita, K.; Mitsudo, T. *J. Am. Chem. Soc.* **1999**, *121*, 482.
8. Arisawa, M.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 763.
9. (a) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902. (b) Bäckvall, J.-E.; Ericsson, A. *J. Org. Chem.* **1994**, *59*, 5850. (c) Ogawa, A.; Kawakami, J.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1996**, *61*, 4161. (d) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108.
10. (a) Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
11. Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 8249.
12. Han, L.-B.; Tanaka, M. *Chem. Lett.* **1999**, 863.
13. Hua, R.; Takeda, H.; Onozawa, S.; Abe, Y.; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 2899.
14. (a) Kondo, T.; Morisaki, Y.; Uenoyama, S.; Wada, K.; Mitsudo, T. *J. Am. Chem. Soc.* **1999**, *121*, 8657. (b) Kondo, T.; Kanda, Y.; Baba, A.; Fukuda, K.; Nakamura, A.; Wada, K.; Morisaki, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **2002**, *124*, 12960.
15. Sugoh, K.; Kuniyasu, H.; Sugae, T.; Ohtaka, A.; Takai, Y.; Tanaka, A.; Machino, C.; Kambe, N.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 5108.
16. (a) Ogawa, A.; Kuniyasu, H.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1997**, *62*, 8361. (b) Gabriele, B.; Salerno, G.; Fazio, A. *Org. Lett.* **2000**, *2*, 351.
17. (a) Holmquist, H. E.; Carnahan, J. E. *J. Org. Chem.* **1960**, *25*, 2240. (b) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147. (c) Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 2609. (d) Shim, S. C.; Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 1935.
18. (a) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *326*, 35. (b) Takahashi, H.; Ohe, K.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *334*, C43.
19. Ogawa, A.; Takeba, M.; Kawakami, J.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1995**, *117*, 7564.
20. Ogawa, A.; Kawakami, J.; Mihara, M.; Ikeda, T.; Sonoda, N.; Hirao, T. *J. Am. Chem. Soc.* **1997**, *119*, 12380.
21. (a) Reppe, V. W. *Liebigs Ann.* **1953**, *582*, 1. (b) Reppe, V. W.; Kröper, H. *Liebigs Ann.* **1953**, *582*, 38.
22. While we discovered the Pt-catalyzed hydrothicarbonylation, the Pd-catalyzed reactions using dppp, etc as an additive to give the product introduced thioester group into acetylenes were reported. (a) Xiao, W.-J.; Alper, H. *J. Org. Chem.* **1997**, *62*, 3422. (b) Xiao, W.-J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1998**, *63*, 2609. (c) Xiao, W.-J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1999**, *64*, 2080. (d) Xiao, W.-J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **2000**, *65*, 4138. (e) Xiao, W.-J.; Alper, H. *J. Org. Chem.* **2001**, *66*, 6229. (f) Ali, B. E.; Tijani, J.; El-Ghanam, A.; Fettouhi, M. *Tetrahedron Lett.* **2001**, *42*, 1567.
23. Ogawa, A.; Kawabe, K.; Kawakami, J.; Mihara, M.; Ikeda, T.; Hirao, T.; Sonoda, N. *Organometallics* **1998**, *17*, 3111.
24. Ugo, R.; La Monica, G.; Cenini, S.; Segre, A.; Conti, F. *J. Chem. Soc. A* **1971**, 522.
25. Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.