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Rhodium-catalyzed highly selective thioformylation of acetylenes with thiols and carbon monoxide

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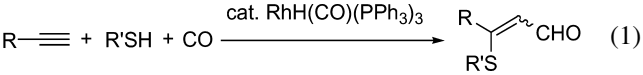
Abstract—Highly regioselective thioformylation of terminal acetylenes with thiols and carbon monoxide has been developed by the use of rhodium(I) complexes as the catalyst: formyl and thio groups are introduced into the terminal and inner positions of acetylenes, respectively. The thioformylation is performed in the presence of a catalytic amount of rhodium(I) complexes, such as $RhH(CO)(PPh_3)_3$, $RhCl(PPh_3)_3$, and $RhCl(CO)(PPh_3)_2$, under the pressure of CO (3 MPa) at 120°C in CH_3CN to provide β-thio-α,β-unsaturated aldehydes in good yields. This thioformylation can be applied to a variety of terminal acetylenes and aromatic thiols. A mechanistic proposal includes the formation of the rhodium sulfide complex as the key species.

1. Introduction

Transition-metal-catalyzed reactions with main group compounds, such as organic silicon,[1] tin,[2] and boron[3] compounds, have been extensively investigated and have been established for effecting a wide range of synthetic reactions. In contrast, the use of organosulfur compounds in transition-metal-catalyzed reactions has been largely unexplored, despite the fact that sulfur compounds easily react with transition metal compounds to give a variety of sulfur-coordinated metal complexes.[4] In general, sulfur compounds are believed to bind strongly to transition metal compounds and therefore make the catalytic reactions ineffective. Perhaps widespread prejudice that 'sulfur compounds are catalyst poisons' has precluded investigation in this area. However, several works concerning transition-metal-catalyzed reactions of sulfur compounds strongly suggested the efficacy of transition-metal-catalyzed synthetic reactions of sulfur compounds.[5,6] For example, we have developed highly selective transition-metal-catalyzed additions of organic thiols or disulfides to acetylenes, providing a series of vinylic sulfides in good yields with excellent regio- and/or stereoselectivities.[5,7] 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.[6k–m] Furthermore, the $Co_2(CO)_8$-catalyzed carbonylation of organic diselenide or ditelluride has been developed by Uemura, Ohe, and co-workers.[8] After these works, a number of transition-metal-catalyzed reactions of various organosulfur compounds have been developed successfully:[1c,9–13] e.g. thioboration,[10] thiosilylation,[11a] thiophosphorylation,[11b] thioesterification,[11c] *S*-propargylation or allylation of thiols,[12b,c] and carbothiolation,[13s] etc.

We have further discovered the first example of $RhH(CO)(PPh_3)_3$-catalyzed 'thioformylation' of acetylenes with thiols and carbon monoxide (Eq. (1)).[14] This thioformylation exhibits the excellent regioselectivity where carbon monoxide and thio groups are introduced selectively into the terminal and inner positions of acetylenes, respectively.



(1)

In this paper, we describe full details of the rhodium-catalyzed carbonylative addition of thiols to acetylenes under the pressure of carbon monoxide. We also report some mechanistic considerations of this carbonylation. This reaction provides a general method for the regioselective introduction of thiols and carbon monoxide into acetylenes.

2. Results and discussion

2.1. $RhCl(PPh_3)_3$-Catalyzed thioformylation of 1-octyne with benzenethiol and carbon monoxide

Our recent investigations on catalytic hydrothiolation

Keywords: thioformylation; rhodium; thiols; carbon monoxide; acetylenes; Wilkinson catalyst.
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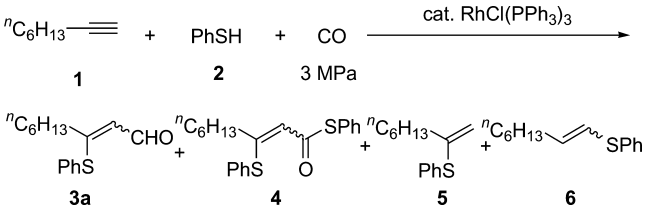
Table 1. Influence of solvent on $RhCl(PPh_3)_3$-catalyzed reaction



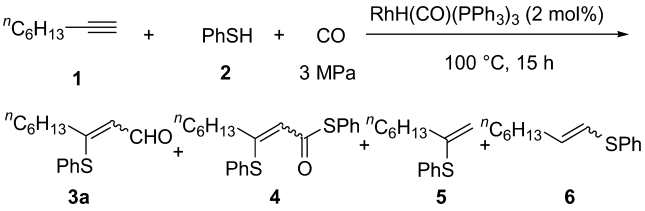
Entry	Solvent	Yield (%)[a]			
		3a (*E*/*Z*)	**4**	**5**	**6**
1	CH_3CN	25 (68/32)	3	Trace	7
2	DME	25 (72/28)	6	4	15
3	HMPA	Trace	2	3	4
4	Dioxane	10 (50/50)	4	Trace	6
5	Toluene	11 (64/36)	11	3	0

Reaction conditions: **1** (1 mmol), **2** (1 mmol), CO (3 MPa), $RhCl(PPh_3)_3$ (2 mol%), solvent (1 mL), 100°C, 15 h.
[a] Determined by ^1H NMR.

reactions have proved that Wilkinson catalyst ($RhCl(PPh_3)_3$) is effective for *anti*-Markovnikov addition of benzenethiol to terminal acetylenes with excellent stereoselectivity (*syn*-addtion).[7] It might be expected that this catalyst also exhibits a catalytic activity toward the desired carbonylative addition reaction of thiols to acetylenes in the presence of carbon monoxide. As mentioned in Table 1, the $RhCl(PPh_3)_3$-catalyzed reaction of 1-octyne (**1**, 1 mmol) with benzenethiol (**2**, 1 mmol) and carbon monoxide (3 MPa) in CH_3CN provided the desired thioformylation product **3a**, although the yield was not so high (entry 1). Next, we investigated this $RhCl(PPh_3)_3$-catalyzed thioformylation in detail by varying the reaction conditions. At first, the influence of the solvents on this thioformylation was examined (Table 1). The reaction in DME gave **3a** in 25% yield (entry 2), but the selectivity was lower compared with those in CH_3CN (entry 1). The use of HMPA, dioxane, and toluene as the solvent resulted in decrease of both the yield and the selectivity (entries 3–5).

Table 2 indicates the $RhCl(PPh_3)_3$-catalyzed carbonylation of 1-octyne with PhSH and CO in CH_3CN under the conditions varying the reaction temperature, reaction time, the pressure of CO, and the molar ratio of acetylene/thiol. As can be seen from entries 1–3, higher temperature (100°C) and prolonged reaction time (42 h) increased the yield of the thioformylation product (**3a**) (34%). Diminishing the CO pressure resulted in the decrease of the yield of **3a** (entries 2 and 4).

Table 3. Influence of solvent on $RhH(CO)(PPh_3)_3$-catalyzed reaction



Entry	Solvent	Yield (%)[a]			
		3a (*E*/*Z*)	**4**	**5**	**6**
1	CH_3CN	41 (56/44)	4	12	2
2	DME	43 (76/24)	6	15	Trace
3	THF	51 (67/33)	9	9	19
4	Pyridine	46 (76/24)	4	35	Trace
5	CH_2Cl_2	13 (77/23)	12	0	0

Reaction conditions: **1** (1 mmol), **2** (1 mmol), CO (3 MPa), $RhH(CO)(PPh_3)_3$ (2 mol%), solvent (1 mL), 100°C, 15 h.
[a] Determined by ^1H NMR.

On the other hand, the increase in the molar ratio of acetylene/thiol (**1/2**) led to the increase in the yield of **3a**. For example, when 3 equiv. of 1-octyne was employed, the desired **3a** was obtained in 63% yield (entry 5). Numerous attempts have been made to optimize the reaction conditions, and finally the yield of **3a** was increased to 70% (*E*/*Z*=68/32) when the $RhCl(PPh_3)_3$-catalyzed reaction was carried out by use of 1.5 equiv. of 1-octyne at 120°C for 20 h under the pressure of CO (3 MPa) (entry 8).

2.2. $RhH(CO)(PPh_3)_3$-Catalyzed thioformylation of acetylenes with thiols and carbon monoxide

As well as $RhCl(PPh_3)_3$, $RhH(CO)(PPh_3)_3$ is found to work as an excellent catalyst for the desired thioformylation of 1-octyne (**1**) with PhSH (**2**) and CO. Table 3 indicates the influence of solvents on this $RhH(CO)(PPh_3)_3$-catalyzed thioformylation. The use of CH_3CN, DME, THF and pyridine as the solvent led to the formation of the thioformylation product **3a** in moderate yields (entries

Table 2. $RhCl(PPh_3)_3$-catalyzed reaction of 1-octyne with benzenethiol and carbon monoxide

Entry	**1/2**	CO (MPa)	Temperature (°C)	Time (h)	Yield (%)[a]			
					3a (*E*/*Z*)	**4**	**5**	**6**
1	1	3	80	36	27 (78/22)	4	6	10
2	1	3	100	15	25 (68/32)	3	Trace	7
3	1	3	100	42	34 (71/29)	9	Trace	7
4	1	1.5	100	15	12 (67/33)	2	Trace	7
5	3	3	100	15	63 (56/44)	6	2	13
6	3	3	100	42	57 (58/42)	6	Trace	7
7[b]	1.5	3	120	5	46 (43/57)	Trace	Trace	Trace
8[b]	1.5	3	120	20	70 (68/32)	Trace	0	Trace
9[b]	1.5	3	120	42	46 (28/72)	4	0	7
10[b]	1.5	3	140	20	42 (26/74)	3	Trace	10

Reaction conditions: **1** (1–3 mmol), **2** (1 mmol), CO (1.5–3 MPa), $RhCl(PPh_3)_3$ (2 mol%), CH_3CN (1 mL).
[a] Determined by ^1H NMR.
[b] $RhCl(PPh_3)_3$ (3 mol%).

Table 4. Influence of reaction temperature on $RhH(CO)(PPh_3)_3$-catalyzed reaction

Entry	Temperature (°C)	Time (h)	Yield (%)[a]			
			3a (*E*/*Z*)	**4**	**5**	**6**
1	100	15	41 (56/44)	4	2	2
2	100	40	35 (71/29)	10	1	7
3[b]	110	15	58 (59/41)	5	5	Trace
4[b]	120	5	57 (71/29)	3	7	Trace
5[b]	120	15	60 (77/23)	2	5	17
6[b]	140	15	41 (39/61)	2	4	3

Reaction conditions: **1** (1 mmol), **2** (1 mmol), CO (3 MPa), $RhH(CO)(PPh_3)_3$ (2 mol%), CH_3CN (1 mL).
[a] Determined by ^1H NMR.
[b] $RhH(CO)(PPh_3)_3$ (3 mol%).

1–4). In particular, the reaction in CH_3CN realized a better selectivity of **3a**. On the other hand, the reaction in pyridine afforded not only **3a** (46%) but also Markovnikov adduct **5** (35%) (entry 4).

Table 4 indicates the influence of the reaction temperature on this thioformylation, and the thioformylation product (**3a**) was found to be formed in 60% yield, when the reaction was carried out under carbon monoxide (3 MPa) at 120°C for 15 h. However, higher temperature (140°C) provided **3a** in only 41% yield.

Furthermore, in the case of higher CO pressure, the yield of the thioformylation product **3a** was increased (Table 5). In particular, the product **3a** was obtained in 78% yield, when the reaction was conducted under 5 MPa of carbon monoxide (entry 4).

Thus, we next investigated the optimization of this thioformylation by employing the excess amounts of acetylenes (Table 6). Although the reaction at 80°C proceeded very slowly (entry 1), higher temperature (100 and 120°C) successfully provided **3a** in 71 and 82% yields, respectively (entries 3 and 14). Much effort has been done to determine the optimized reaction conditions, and finally $RhH(CO)(PPh_3)_3$ is found to be an excellent catalyst for the thioformylation of 1-octyne with benzenethiol and carbon monoxide (**1**/**2**=1.5, 120°C, 5 h, 3 MPa, see entry 14). The $RhH(CO)(PPh_3)_3$-catalyzed thioformylation was also sensitive to the reaction concentration. In the cases of both higher and lower reaction concentrations, the yield was decreased (entries 5, 8, 9, 12, and 13).

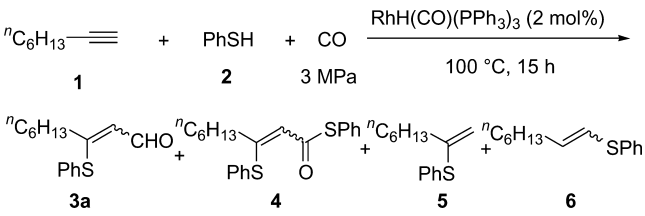
With respect to the stereoisomers of **3a** (*Z* and *E*), the *Z* isomer was a kinetic product and was gradually isomerized

Table 5. Influence of CO pressure on $RhH(CO)(PPh_3)_3$-catalyzed reaction

Entry	CO (MPa)	Yield (%)[a]			
		3a (*E*/*Z*)	**4**	**5**	**6**
1	1	49 (29/71)	6	4	10
2	1.5	71 (20/80)	5	14	Trace
3	3	72 (69/31)	8	4	Trace
4	5	78 (38/62)	6	6	Trace

Reaction conditions: **1** (3 mmol), **2** (1 mmol), CO (1–5 MPa), $RhH(CO)(PPh_3)_3$ (2 mol%), CH_3CN (1 mL), 100°C, 15 h.
[a] Determined by ^1H NMR.

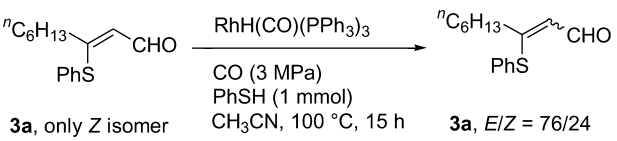
Table 6. $RhH(CO)(PPh_3)_3$-Catalyzed reaction of 1-octyne with benzenethiol and carbon monoxide



Entry	**1**/**2**	Temperature (°C)	Time (h)	Yield (%)[a]			
				3a (*E*/*Z*)	**4**	**5**	**6**
1	3	80	15	24 (67/33)	4	1	Trace
2	3	100	3	44 (30/70)	5	7	Trace
3	3	100	5	71 (23/77)	9	11	Trace
4	3	100	15	72 (69/31)	8	4	Trace
5[b]	3	100	15	69 (84/16)	7	5	Trace
6[c]	3	100	15	62 (27/73)	7	6	Trace
7	1.5	100	15	51 (67/33)	6	4	Trace
8[d]	1.5	100	15	45 (62/38)	4	2	5
9[e]	1.5	100	15	49 (67/33)	7	8	Trace
10	1.5	110	5	64 (23/77)	4	11	Trace
11	1.5	110	7	72 (21/79)	2	10	Trace
12[b]	1.5	110	6	50 (12/88)	1	6	0
13[e]	1.5	110	7	63 (40/60)	4	11	Trace
14	1.5	120	5	82 (13/87)	0	10	Trace
15	1.5	10	5	23 (26/74)	2	1	4

Reaction conditions: **1** (1.5–3 mmol), **2** (1 mmol), CO (3 MPa), $RhH(CO)(PPh_3)_3$ (entries 1–5, 7–9; 2 mol%, entries 10–14; 3 mol%), CH_3CN (1 mL).
[a] Determined by ^1H NMR.
[b] CH_3CN (3 mL).
[c] $RhH(CO)(PPh_3)_3$ (1 mol%).
[d] CH_3CN (2 mL).
[e] CH_3CN (0.5 mL).

to thermodynamically more stable *E* isomer during the reaction (entries 2–5 and 7–14). For example, the *E*/*Z* ratio of **3a** was 23/77 in the reaction at 100°C for 5 h, whereas the *E*/*Z* ratio changed to 69/31 when the reaction continued for additional 10 h (entries 3 and 4). Interestingly, however, when the amount of catalyst was decreased, the reaction gave *Z* isomer preferentially despite the reaction time was 15 h (entry 6). By using the thioformylation product **3a** (*Z* only) formed from 1-octyne, isomerization (*Z*)-**3a** to (*E*)-**3a** was examined under the thioformylation reaction conditions (Eq. (2)). As a result, isomerization of *Z* to *E* occurred with relative ease (*E*/*Z* ratio of **3a** was 76/24).



(2)

Table 7 indicates the influence of additives on the $RhH(CO)(PPh_3)_3$-catalyzed thioformylation. Although the addition of Et_3N to the rhodium-catalyzed silylformylation was reported to improve the reaction rate and the yield of the product,[15] the present thioformylation was sharply retarded (entry 1). The addition of water (1 equiv.) did not affect the thioformylation (entry 2). Interestingly, the use of $RhH(CO)(PPh_3)_3$ with $P(OPh)_3$ led to the increase of the yield of the product **3a**, while the reaction with dppe was less effective (entries 3 and 4).

Table 7. Influence of additives on $RhH(CO)(PPh_3)_3$-catalyzed thioformylation

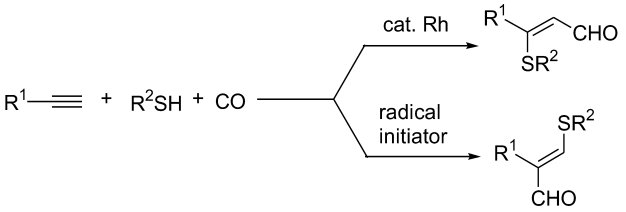
Entry	1/2	Additive	Yield (%)[a]			
			3a (*E*/*Z*)	**4**	**5**	**6**
1	1	Et_3N (4 mol%)	Trace	2	2	0
2	3	H_2O (1 equiv.)	57 (46/54)	6	2	Trace
3	1.5	$P(OPh)_3$ (4 mol%)	68 (78/22)	6	Trace	Trace
4	1.5	dppe (3 mol%)	40 (50/50)	7	4	Trace
5	1.5	None	51 (67/33)	6	4	Trace

Reaction conditions: **1** (1–3 mmol), **2** (1 mmol), CO (3 MPa), $RhH(CO)(PPh_3)_3$ (2 mol%), CH_3CN (1 mL), 100°C, 15 h.
[a] Determined by ^1H NMR.

As mentioned already, the thioformylation product **3a** was obtained in high yield when the $RhCl(PPh_3)_3$ or $RhH(CO)(PPh_3)_3$-catalyzed reaction was carried out using 1-octyne (1.5 equiv.) under 3 MPa of carbon monoxide at 120°C (Table 8, entries 1 and 2). However, the $RhCl(PPh_3)_3$-catalyzed thioformylation required prolonged reaction time (20 h), compared with the $RhH(CO)(PPh_3)_3$-catalyzed one. This is most probably because $RhH(CO)(PPh_3)_3$ can easily generate the active catalyst ($Rh(SPh)(CO)(PPh_3)_2$) with the evolution of molecular hydrogen (see; Eq. (4)), and $RhCl(PPh_3)_3$ might require longer time to produce the active catalyst. We also examined the reaction using $RhCl(CO)(PPh_3)_2$ and $[Rh(CO)_2Cl]_2$ as the catalyst under the above optimized conditions. The $RhCl(CO)(PPh_3)_2$-catalyzed thioformylation took place regioselectively to provide **3a** in good yield. On the other hand, $[Rh(CO)_2Cl]_2$ was ineffective (entry 4). These results suggest that the presence of phosphine ligands is important in this thioformylation.

Table 9 summarizes the representative results of the $RhH(CO)(PPh_3)_3$-catalyzed thioformylation using various thiols and terminal acetylenes. The thioformylation with aromatic thiols such as *p*-fluorobenzenethiol and *p*-methylbenzenethiol proceeded smoothly to give the corresponding products **3b** and **3c** in good yield, respectively (entries 2 and 3). However, the thioformylation of aliphatic thiols like dodecanethiol required prolonged reaction time, providing **3d** in low yield (entry 4). Aliphatic acetylenes can be employed as the substrates for this thioformylation successfully (entries 5, 6, 8–10). Functionalities such as OH and CN are tolerant to this thioformylation (entries 6 and 9). Although the thioformylation of aromatic acetylenes took place regioselectively, the Markovnikov adduct of benzenethiol **7** was also produced in 28% yield (entry 7).

Starting from the same substrates (i.e. acetylene, thiol, and CO), the thioformylation via a radical pathway was reported, which indicated the different regioselectivity, i.e. thio and formyl groups are introduced into terminal and inner positions of terminal acetylenes: PhS·attacks the terminal carbon of alkynes to give β-alkylthio alkenyl radical and then the reaction of this radical with carbon monoxide followed by hydrogen abstraction from thiol give the regioselective thioformylation products (Eq. (3)).[16] Accordingly, both methods, i.e. the rhodium-catalyzed and the radical-mediated thioformylations, are complementary to each other for regioselective synthesis of β-thio-α,β-unsaturated aldehydes from acetylenes.



(3)

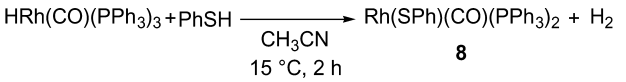
Table 8. Rhodium-catalyzed thioformylation of 1-octyne with benzenethiol and carbon monoxide

Entry	Catalyst	**3a**, yield (%)[a]	*E*/*Z*
1	$RhH(CO)(PPh_3)_3$	82	13/87
2	$RhCl(PPh_3)_3$	46 (70[b])	43/57 (68/32[b])
3	$RhCl(CO)(PPh_3)_2$	68	39/61
4	$[Rh(CO)_2Cl]_2$	19	57/43

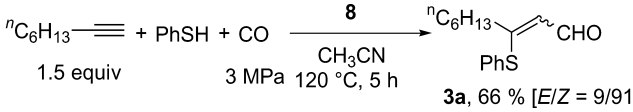
Reaction conditions: **1** (7.5 mmol), **2** (5 mmol), CO (3 MPa), Rh catalyst (3 mol%), CH_3CN (5 mL), 120°C, 5 h.
[a] Determined by ^1H NMR.
[b] Reaction time: 20 h.

2.3. Mechanistic considerations of $RhH(CO)(PPh_3)_3$-catalyzed thioformylation of acetylenes with thiols and carbon monoxide

To get insight into the reaction pathway for this thioformylation, stoichiomertric reaction of $RhH(CO)(PPh_3)_3$ with benzenethiol was examined. The equimolar reaction of $RhH(CO)(PPh_3)_3$ with PhSH at 15°C in acetonitrile under argon atmosphere afforded a yellow solid (**8**) with the evolution of molecular hydrogen. ^1H NMR spectra indicated the disappearance of the signal at δ −9.71 assigned to the hydride of $RhH(CO)(PPh_3)_3$.[17] The IR spectra of the yellow solid showed that the CO absorption (1922 cm^{-1})[17] of $RhH(CO)(PPh_3)_3$ disappeared and new carbonyl absorption appeared at 1969 cm^{-1}. These results and elemental analysis of the yellow solid indicate unambiguously that the formed complex is $Rh(SPh)(CO)(PPh_3)_2$ (Eq. (4)).[18] The catalytic reaction of 1-octyne (**1**) with benzenethiol and CO in the presence of 3 mol% of complex **8** afforded the thioformylation product **3a** in good yield (Eq. (5)).



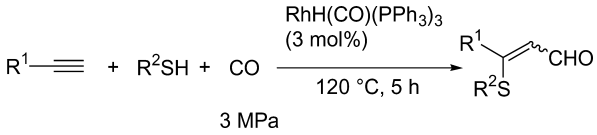
(4)



(5)

On the other hand, the reaction of $RhH(CO)(PPh_3)_3$ with excess amounts of PhSH (5 equiv.) at 15°C in acetonitrile under argon atmosphere gave a brown solid (**8′**). The reaction of 1-octyne (**1**) with benzenethiol and CO in the presence of 3 mol% of complex **8′** did not provide **3a**. These results indicate that complex **8′** has no catalytic activity toward the thioformylation. Accordingly, the complex **8**

Table 9. $RhH(CO)(PPh_3)_3$-Catalyzed thioformylation of acetylenes with thiols and carbon monoxide

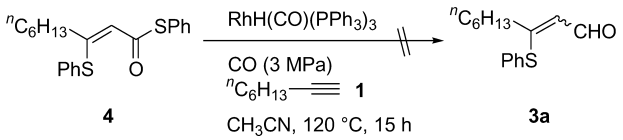


Entry	Acetylene R^1	Thiol R^2	Product **3**	
			Isolated yield (%)	*E*/*Z*
1	$^nC_6H_{13}$	Ph	**3a** (82)	13/87
2		*p*-F-C_6H_4	**3b** (76)	24/76
3		*p*-Me-C_6H_4	**3c** (72)	31/69
4		$CH_3(CH_2)_{11}$	**3d** (27)	41/59
5	$(CH_3)_2CH(CH_2)_2$	Ph	**3e** (80)	14/86
6	$HO(CH_2)_3$		**3f** (76)	86/14
7	Ph		**3g** (52)	16/84
8	$PhCH_2$		**3h** (63)	54/46
9	$NC(CH_2)_3$		**3i** (61)	23/77
10	$\equiv CH_2(CH_2)_3$		**3j** (58)	1/99

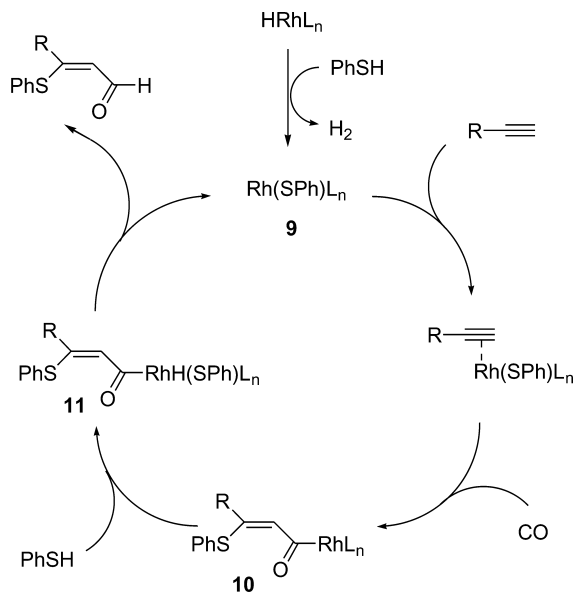
Reaction conditions: acetylene (7.5 mmol), thiol (5 mmol), CO (3 MPa), $RhH(CO)(PPh_3)_3$ (3 mol%), CH_3CN (5 mL), 120°C, 5 h.

formed at the initial stage may act as an active catalyst in a catalytic cycle of thioformylation.

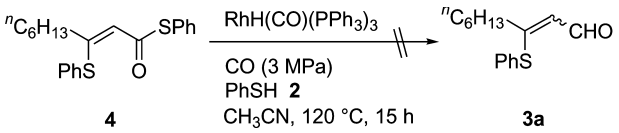
Since the $RhH(CO)(PPh_3)_3$-catalyzed thioformylation gave **4** (2–10%) as a byproduct, the reaction of **4** with 1-octyne under 3 MPa of carbon monoxide in the presence of $RhH(CO)(PPh_3)_3$ (3 mol%) at 120°C for 15 h was examined. However, the attempted reaction did not afford the thioformylation product **3a** (Eq. (6)).[19] The use of benzenethiol, instead of 1-octyne, resulted in the recovery of **4** (Eq. (7)).



(6)

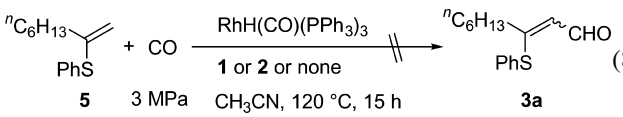


Scheme 1.



(7)

Moreover, the reaction of **5** under 3 MPa of carbon monoxide in the presence of $RhH(CO)(PPh_3)_3$ (3 mol%) at 120°C for 15 h did not provide **3a** (Eq. (8)). These results suggest that both **4** and **5** are not precursors for this thioformylation product **3a**.



(8)

A plausible mechanism for this thioformylation is shown in Scheme 1. The reaction includes the formation of the rhodium sulfide complex **9** as the key species. Acetylenes coordinate to the complex and then undergo regioselective thiorhodation to give the vinylic rhodium complex **10**. The CO-insertion to give the acylrhodium complex **11**, followed by the reaction with PhSH affords the thioformylation product with regeneration of the rhodium sulfide complex **9**.

3. Conclusion

In summary, we have developed a highly selective thioformylation of acetylenes with thiols and carbon monoxide. In this reaction, the excellent regioselectivity is observed: thio and formyl groups are introduced selectively into the inner and terminal carbons of terminal acetylenes, respectively. Thioformylation compounds could be produced in good yields in the presence of a catalytic amount of rhodium(I) complexes, such as $RhH(CO)(PPh_3)_3$, $RhCl(PPh_3)_3$, and $RhCl(CO)(PPh_3)_2$. The results in this paper clearly demonstrate that transition-metal catalysts are very useful for the synthetic reactions of sulfur compounds.

4. Experimental

4.1. General comments

^{1}H NMR spectra were recorded on JEOL JNM-GSX-270 (270 MHz) and JEOL JNM-AL400 (400 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) and JEOL JNM-AL400 (100 MHz) spectrometers using $CDCl_3$ as the solvent. Chemical shifts in ^{13}C NMR were measured relative to $CDCl_3$ and converted to δ (Me_4Si) value by using δ ($CDCl_3$)=76.9 ppm. IR spectra were determined on a Perkin–Elmer Model 1600 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Mass spectra were obtained on JEOL JMS-DX303 in the analytical section of our department. Elemental analyses were also performed there. All materials were obtained from commercial supplies and purified by distillation or recrystallization. Compounds **4**–**7** have been identified by comparison with the literature data.[5,7]

4.2. General procedure for the $RhH(CO)(PPh_3)_3$-catalyzed thioformylation of acetylenes with carbon monoxide and thiols

In a 50 mL stainless steel autoclave with a magnetic stirring bar under argon atmosphere were placed $RhH(CO)(PPh_3)_3$ (3 mol%), acetonitrile (5 mL), acetylene (7.5 mmol), and thiol (5 mmol). Carbon monoxide was purged for three times and then charged at 3 MPa. The reaction was conducted with magnetic stirring for 5 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 hexane/Et_2O=4/1).

4.2.1. 3-Phenylthio-2-nonenal (3a). [*Z* isomer] yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (t, *J*=6.8 Hz, 3H), 1.23–1.25 (m, 6H), 1.46 (quint., *J*=7.4 Hz, 2H), 2.22 (t, *J*=7.4 Hz, 2H), 6.18 (d, *J*=7.8 Hz, 1H), 7.37–7.49 (m, 5H), 10.15 (d, *J*=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.4, 28.4, 28.6, 31.3, 37.1, 127.7, 129.0, 129.4, 130.7, 134.0, 164.4, 190.1; IR (NaCl) 2928, 2856, 1670, 1571, 1535, 1477, 1150, 749, 692 cm^{-1}; MS (EI), *m*/*z*=248 (M^+, 65). Anal. calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12. Found: C, 72.61; H, 8.26. [*E* isomer] yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, *J*=6.6 Hz, 3H), 1.29–1.47 (m, 6H), 1.75 (quint., *J*=7.7 Hz, 2H), 2.78 (t, *J*=7.7 Hz, 2H), 5.42 (d, *J*=7.8 Hz, 1H), 7.37–7.48 (m, 5H), 9.78 (d, *J*=7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.5, 28.9, 31.1, 31.4, 32.6, 121.9, 128.5, 129.9, 130.3, 135.6, 171.0, 186.8; IR (NaCl) 3059, 2955, 2929, 2746, 1661, 1580, 1557, 1150, 751, 691 cm^{-1}; MS (EI), *m*/*z*=248 (M^+, 66); HRMS calcd for $C_{15}H_{20}OS$ 248.1235, found 248.1225.

4.2.2. 3-*p*-Fluoro(phenylthio)-2-nonenal (3b). [*Z* isomer] yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.84 (t, *J*=7.1 Hz, 3H), 1.13–1.26 (m, 6H), 1.44 (quint., *J*=7.3 Hz, 2H), 2.18 (t, *J*=7.6 Hz, 2H), 6.16 (d, *J*=6.8 Hz, 1H), 7.06–7.14 (m, 2H), 7.44–7.50 (m, 2H), 10.13 (d, *J*=6.4 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.4, 28.4, 28.6, 31.3, 36.9, 116.7 (d, *J*=23 Hz), 125.7, 127.1, 136.4 (d, *J*=8.3 Hz), 163.4 (d, *J*=250 Hz), 164.2, 189.8; IR (NaCl) 2955, 2930, 2858, 1671, 1590, 1575, 1538, 1490, 1467, 1226, 1157, 1092, 835, 816 cm^{-1}; MS (EI), *m*/*z*=266 (M^+, 32). Anal. calcd for $C_{15}H_{19}FOS$: C, 67.64; H, 7.19. Found: C, 67.80; H, 7.28. [*E* isomer] Purification of (*E*)-**2a′** by MPLC resulted in the formation of a *E*/*Z* mixture of **2a′** (9/1) due to similar polarities of the *E* and *Z* isomers. The following spectral date were therefore obtained by using the *E* and *Z*-mixture: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, *J*=6.6 Hz, 3H), 1.30–1.44 (m, 6H), 1.75 (quint., *J*=7.6 Hz, 2H), 2.78 (t, *J*=7.8 Hz, 2H), 5.36 (d, *J*=7.8 Hz, 1H), 7.09–7.17 (m, 2H), 7.43–7.48 (m, 2H), 9.78 (d, *J*=7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.5, 28.9, 31.1, 31.4, 32.5, 117.3 (d, *J*=23 Hz), 121.9, 123.8, 137.8 (d, *J*=8.4 Hz), 164.0 (d, *J*=253 Hz), 171.0, 186.9.

4.2.3. 3-*p*-Methyl(phenylthio)-2-nonenal (3c). [*Z* isomer] yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (t, *J*=6.8 Hz, 3H), 1.12–1.30 (m, 6H), 1.44 (m, 2H), 2.19 (t, *J*=7.8 Hz, 2H), 2.37 (s, 3H), 6.14 (d, *J*=6.8 Hz, 1H), 7.18 (d, *J*=7.8 Hz, 2H), 7.32 (d, *J*=7.8 Hz, 2H), 10.14 (d, *J*=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 21.2, 22.4, 28.4, 28.6, 31.3, 36.9, 126.8, 126.9, 130.2, 134.3, 139.5, 165.2, 189.8; IR (NaCl) 3023, 2955, 2928, 2858, 2734, 1671, 1575, 1537, 1492, 1456, 1381, 1150, 1090, 1018, 811, 725, 673 cm^{-1}; MS (EI), *m*/*z*=262 (M^+, 49). Anal. calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45. Found: C, 73.14; H, 8.53. [*E* isomer] yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, *J*=6.8 Hz, 3H), 1.33–1.39 (m, 6H), 1.75 (quint., *J*=7.4 Hz, 2H), 2.39 (s, 3H), 2.77 (t, *J*=7.8 Hz, 2H), 5.39 (d, *J*=8.1 Hz, 1H), 7.23 (d, *J*=8.1 Hz, 2H), 7.34 (d, *J*=8.1 Hz, 2H), 9.77 (d, *J*=8.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 21.4, 22.5, 29.0, 31.2, 31.5, 32.6, 121.8, 124.6, 130.8, 135.5, 140.7, 171.6, 187.0; IR (NaCl) 3024, 2955, 2927, 2857, 2745, 1660, 1582, 1557, 1493, 1463, 1456, 1394, 1180, 1150, 1119, 1018, 846, 812, 707 cm^{-1}; MS (EI), *m*/*z*=262 (M^+, 20). Anal. calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45. Found: C, 73.93; H, 8.53.

4.2.4. 3-Dodecylthio-2-nonenal (3d). [*E*/*Z* mixture] yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86–0.90 (m, 6H), 1.18–1.26 (m, 24H), 1.59–1.69 (m, 4H), 2.43–2.85 (m, 4H), 6.06 (d, *J*=6.9 Hz, 1H), 10.06 (d, *J*=6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.4, 28.3, 28.4, 29.0, 29.1, 29.3, 31.3, 31.6, 36.6, 39.0. 126.9, 165.5, 189.9; IR (NaCl) 2924, 2853, 1672, 1466, 1439, 721, 505 cm^{-1}; MS (EI), *m*/*z*=339 (M^+, 10.2); HRMS calcd for $C_{21}H_{20}OS$ 340.2803, found 340.2802.

4.2.5. 6-Methyl-3-phenylthio-2-heptenal (3e). [*Z* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.72 (d, *J*=6.3 Hz, 6H), 1.33–1.35 (m, 3H), 2.22 (t, *J*=7.6 Hz, 2H), 6.18 (d, *J*=6.8 Hz, 1H), 7.39–7.48 (m, 5H), 10.14 (d, *J*=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.1, 27.5, 35.1, 38.0, 127.4, 129.1, 129.4, 130.5, 134.1, 164.9, 190.0; IR (NaCl) 3059, 2955, 2930, 2869, 1670, 1581, 1572, 1538, 1468, 1440, 1385, 1156, 1097, 1069, 1023, 749, 704, 692 cm^{-1}; MS (EI), *m*/*z*=234 (M^+, 10.1). Anal. calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.74; H, 7.88. [*E* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.97 (d, *J*=5.9 Hz, 6H), 1.63–1.72 (m, 3H), 2.78 (t, *J*=7.8 Hz, 2H), 5.40 (d, *J*=7.8 Hz, 1H), 7.45–7.46 (m, 5H),

9.79 (d, J=7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.3, 28.1, 30.7, 40.5, 121.5, 128.4, 129.9, 130.3, 135.6, 171.5, 186.8; IR (NaCl) 3058, 2956, 2930, 2869, 2745, 1661, 1579, 1555, 1474, 1468, 1441, 1152, 1121, 848, 751, 706, 691 cm^{-1}; MS (EI), m/z=234 (M^+, 23). Anal. calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.45; H, 7.74.

4.2.6. 6-Hydroxy-3-phenylthio-2-hexenal (3f). [*Z* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.56 (br s, 1H), 1.72 (quint., J=7.6 Hz, 2H), 2.36 (t, J=7.6 Hz, 2H), 3.53 (t, J=7.6 Hz, 2H), 6.22 (d, J=6.8 Hz, 1H), 7.39–7.48 (m, 5H), 10.16 (d, J=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 31.4, 33.4, 61.4, 128.2, 129.2, 129.5, 134.0, 190.0; IR (NaCl) 3402, 2930, 1667, 1652, 1573, 1538, 1476, 1440, 1385, 1143, 1054, 749, 692 cm^{-1}; MS (EI), m/z=222 (M^+, 3.4). Anal. calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35. Found: C, 64.87; H, 6.65. [*E* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.66 (br s, 1H), 2.01 (quint., J=7.3 Hz, 2H), 2.95 (t, J=7.3 Hz, 2H), 3.76 (t, J=5.9 Hz, 2H), 5.47 (d, J=6.8 Hz, 1H), 7.46 (m, 5H), 9.76 (d, J=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 28.9, 33.3, 61.1, 122.0, 130.0, 130.4, 135.6, 187.3; IR (NaCl) 3420, 3058, 2931, 2872, 2360, 1651, 1574, 1475, 1441, 1397, 1281, 1148, 1068, 982, 918, 840, 752, 706, 691 cm^{-1}; MS (EI), m/z=222 (M^+, 2.9); HRMS calcd for $C_{12}H_{14}O_2S$ 222.0715, found 222.0728.

4.2.7. 3-Phenyl-3-phenylthio-2-propenal (3g). [*Z* isomer] yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.55 (d, J=6.8 Hz, 1H), 7.01–7.31 (m, 8H), 7.50–7.54 (m, 2H), 10.32 (d, J=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 127.5, 128.4, 128.7, 129.0, 130.4, 131.25, 131.33, 132.5, 137.1, 159.1, 190.4; IR (NaCl) 3058, 2834, 1666, 1581, 1557, 1488, 1130, 765, 744, 691 cm^{-1}; MS (EI), m/z=240 (M^+, 100). Anal. calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03; S, 13.34. Found: C, 74.74; H, 4.87; S, 13.39. [*E* isomer] yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.67 (d, J=7.8 Hz, 1H), 7.45–7.58 (m, 10H), 9.27 (d, J=7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 123.4, 128.6, 128.9, 129.5, 130.1, 130.3, 130.4, 134.7, 135.4, 169.1, 190.0; IR (NaCl) 3058, 1762, 1711, 1659, 1579, 1563, 1442, 1168, 1128, 909, 750, 735, 692 cm^{-1}; MS (EI), m/z=240 (M^+, 32); HRMS calcd for $C_{15}H_{12}OS$ 240.0609, found 240.0613.

4.2.8. 4-Phenyl-3-phenylthio-2-butenal (3h). [*Z* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.52 (s, 2H), 6.07 (d, J=6.3 Hz, 1H), 6.97–7.41 (m, 10H), 10.15 (d, J=6.3 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 43.3, 127.1, 128.6, 128.7, 129.0, 129.3, 129.4, 130.2, 134.4, 136.4, 162.5, 189.9; IR (NaCl) 3060, 3028, 2828, 1669, 1571, 1536, 1494, 1476, 1453, 1440, 1136, 1069, 748, 696 cm^{-1}; MS (EI), m/z=254 (M^+, 62). Anal. calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55. Found: C, 75.62; H, 5.61. [*E* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.14 (s, 2H), 5.58 (d, J=7.8 Hz, 1H), 7.33–7.44 (m, 10H), 9.88 (d, J=7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 37.9, 122.9, 127.2, 128.3, 128.9, 129.0, 130.0, 130.4, 135.6, 137.2, 167.9, 187.2; IR (NaCl) 3060, 3028, 2849, 2750, 1658, 1579, 1559, 1495, 1475, 1453, 1440, 1142, 750, 728, 692 cm^{-1}; MS (EI), m/z=254 (M^+, 60). Anal. calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55. Found: C, 75.28; H, 5.69.

4.2.9. 6-Cyano-3-phenylthio-2-hexenal (3i). [*Z* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.83 (quint., J=7.3 Hz, 2H), 2.25 (t, J=7.1 Hz, 2H), 2.41 (t, J=7.3 Hz, 2H), 6.23 (d, J=6.4 Hz, 1H), 7.42–7.50 (m, 5H), 10.16 (d, J=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.1, 24.1, 35.4, 118.5, 128.8, 129.4, 129.6, 129.8, 133.8, 160.5, 189.6; IR (NaCl) 3058, 2940, 2834, 2246, 1669, 1582, 1572, 1538, 1477, 1456, 1440, 1385, 1175, 1138, 1078, 1024, 751, 704, 693 cm^{-1}; MS (EI), m/z=231 (M^+, 20); HRMS calcd for $C_{13}H_{13}NOS$ 231.0718, found 231.0715. [*E* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.12 (quint., J=7.3 Hz, 2H), 2.51 (t, J=7.1 Hz, 2H), 2.97 (t, J=7.6 Hz, 2H), 5.51 (d, J=6.8 Hz, 1H), 7.48 (m, 5H), 9.73 (d, J=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.7, 26.1, 31.3, 118.7, 122.3, 129.3, 130.1, 130.6, 135.5, 167.0, 186.2; IR (NaCl) 3058, 2938, 2857, 2247, 1765, 1657, 1580, 1556, 1475, 1441, 1182, 1144, 753, 733, 706, 692 cm^{-1}; MS (EI), m/z=231 (M^+, 21); HRMS calcd for $C_{13}H_{13}NOS$ 231.0718, found 231.0715.

4.2.10. 3-Phenylthio-2-nonen-8-ynal (3j). [*Z* isomer] a pale red-brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.39 (quint., J=7.3 Hz, 2H), 1.60 (quint., J=7.4 Hz, 2H), 1.93 (t, J=2.7 Hz, 1H), 2.06–2.12 (t-d, J=4.4, 2.4 Hz, 2H), 2.25 (t, J=7.6 Hz, 2H), 6.19 (d, J=6.8 Hz, 1H), 7.39–7.49 (m, 5H), 10.15 (d, J=6.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.0, 27.4, 27.6, 36.5, 68.7, 83.7, 127.8, 129.1, 129.4, 130.4, 134.0, 163.6, 190.0; IR (NaCl) 3296, 2940, 2861, 1667, 1652, 1574, 1538, 1478, 1462, 1441, 1384, 1167, 1133, 751, 623 cm^{-1}; MS (EI), m/z=244 (M^+, 0.7); HRMS calcd for $C_{15}H_{16}OS$ 244.0922, found 244.0949. [*E* isomer] yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.66 (quint., J=7.6 Hz, 2H), 1.90 (quint., J=7.3 Hz, 2H), 1.99 (t, J=2.5 Hz, 1H), 2.25–2.30 (t–d, J=4.4, 2.9 Hz, 2H), 2.83 (t, J=7.6 Hz, 2H), 5.43 (d, J=8.0 Hz, 1H), 7.45–7.46 (m, 5H), 9.79 (d, J=7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.1, 27.8, 30.0, 32.0, 69.0, 83.6, 122.0, 128.3, 130.0, 130.3, 135.6, 170.4, 186.8; IR (NaCl) 3300, 2941, 2861, 1658, 1652, 1580, 1475, 1459, 1441, 1168, 1142, 753, 733, 691, 639 cm^{-1}; MS (EI), m/z=244 (M^+, 0.5); HRMS calcd for $C_{15}H_{16}OS$ 244.0922, found 244.0935.

4.3. Procedure for the synthesis of complex 8

In a two-necked flask equipped with a magnetic stirring bar under an argon atmosphere were placed $RhH(CO)(PPh_3)_3$ (135 mg, 1.47 mmol), acetonitrile (3 mL), and benzenethiol (16.3 mg, 1.48 mmol). The mixture was stirred for 2 h at 15°C. The precipitate was filtered and washed with acetonitrile to give $Rh(SPh)(CO)(PPh_3)_2$ (**8**) (93.2 mg) as a yellow solid. Complex **8**. Anal. calcd for $C_{43}H_{37}OP_2RhS$: C, 65.99; H, 4.76; S, 4.10. Found: C, 65.80; H, 4.69; S, 4.10.

4.4. Procedure for thioformylation of 1-octyne with carbon monoxide and thiols by using complex 8

In a 50 mL stainless steel autoclave with a magnetic stirring bar under argon atmosphere were placed complex **8** (47.5 mg, 3 mol%), acetonitrile (2 mL), 1-octyne (312 mg, 2.8 mmol), and benzenethiol (213 mg, 1.9 mmol). Carbon monoxide was purged for three times and then charged at 3 MPa. The reaction was conducted with magnetic stirring for 5 h upon heating at 120°C. After carbon monoxide was purged, the resulting mixture was filtered through Celite and

concentrated in vacuo to afford **3a** (66%, determined by ^{1}H NMR).

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