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Transition-metal-catalyzed carbonylation of allenes with carbon monoxide and thiols

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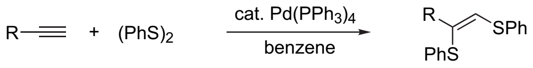
Abstract—In the presence of a catalytic amount of tetrakis(triphenylphosphine)platinum(0), allenes undergo carbonylative thiolation with carbon monoxide and thiols to provide the corresponding α,β- and β,γ-unsaturated thioesters in good yields. In contrast, the use of rhodium(I) catalysts such as $RhH(CO)(PPh_3)_3$ in place of $Pt(PPh_3)_4$ leads to copolymerization of allenes and carbon monoxide without incorporation of thio groups.

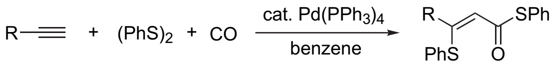
1. Introduction

The transition-metal-catalyzed carbonylation of carbon–carbon unsaturated compounds involving the simultaneous manipulation of heteroatom functions has received a great deal of attention, because synthetically useful heterofunctionalized carbonyl compounds can be easily obtained in one portion.[1] Along this line, carbonylative silylation,[2] amination,[3] and alkoxylation[4] of carbon–carbon unsaturated compounds have been studied intensively. In contrast, the corresponding carbonylative thiolation of unsaturated compounds has been largely unexplored, because organosulfur compounds are generally believed to be catalyst poisons.[5]

Recently, we have developed a series of transition-metal-catalyzed addition/carbonylative addition of organic disulfides and thiols to acetylenes in the absence/presence of carbon monoxide, as depicted in Eqs. 1–4. For example, $Pd(PPh_3)_4$ catalyzes bisthiolation and carbonylative thiolation of acetylenes with disulfides in the absence/presence of carbon monoxide with excellent stereo- and regioselectivities (Eqs. 1 and 2).[6]



(1)



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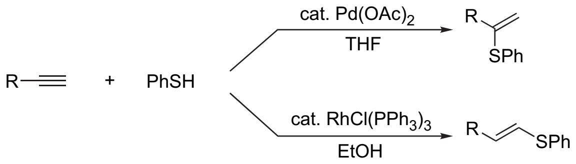
As to the addition of thiols to acetylenes, the regioselectivity of the addition can be controlled easily by the selection of the catalyst: the $Pd(OAc)_2$-catalyzed reaction of acetylenes with thiols provides the corresponding Markovnikov adducts,[7] whereas the use of Wilkinson's catalyst ($RhCl(PPh_3)_3$) leads to the formation of *anti*-Markovnikov adducts, regioselectively (Eq. 3).[8]



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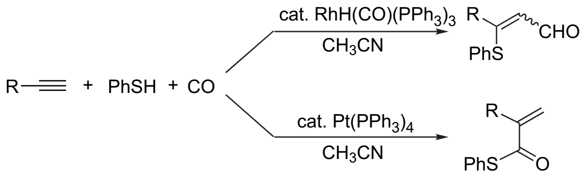

(4)

Furthermore, highly selective thioformylation[9] and hydrothiocarbonylation[10] of acetylenes with carbon monoxide and thiols are able to take place successfully in the presence of rhodium(I) and platinum(0) catalysts, respectively (Eq. 4).

Keywords: Carbonylative thiolation; Thiol; Allene; Carbon monoxide; Copolymerization.

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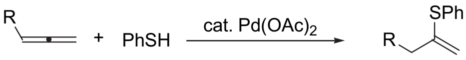
Compared to the transition-metal-catalyzed reactions with acetylenes, transition-metal-catalyzed addition of organosulfur compounds to carbon–carbon double bonds is little known.[11] We have found that the addition of thiols to allenes successfully proceeds regioselectively at the internal double bonds by the action of palladium acetate catalyst (Eq. 5).[12]



(5)

In the course of our studies on the transition-metal-catalyzed carbonylative thiolation, we have investigated the transition-metal-catalyzed carbonylation of allenes as activated carbon–carbon double bond compounds.[13–15]

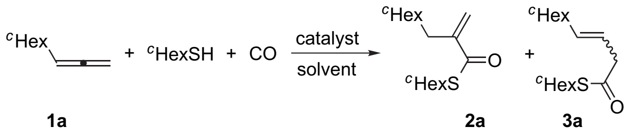
2. Results and discussion

2.1. Platinum-catalyzed carbonylative thiolation of allenes with thiols and carbon monoxide

We initiated the reaction of cyclohexanethiol (^{c}HexSH) with cyclohexylallene under the pressure of carbon monoxide by varying the transition-metal catalysts and solvents (Table 1).

$Pd(PPh_3)_4$ in benzene exhibited no catalytic activity towards the desired carbonylative thiolation, and a simple thiol addition product to the internal double bond of the allene ($^cHexCH_2C(S^cHex){=}CH_2$) was obtained as the major product in 40% yield (Entry 1). $Pd(OAc)_2$ in THF, $RhCl(PPh_3)_3$ in EtOH, $RhH(CO)(PPh_3)_3$ in CH_3CN, and $Co_2(CO)_8$ in CH_3CN also did not catalyze the carbonylative thiolation (Entries 2–5). On the other hand, platinum catalysts such as $PtCl_2(PPh_3)_2$ and $Pt(PPh_3)_4$ in CH_3CN play a good catalyst for the carbonylative thiolation of the allene. For example, the $PtCl_2(PPh_3)_2$-catalyzed carbonylative thiolation of cyclohexylallene with carbon monoxide and ^{c}HexSH proceeded regioselectively at the terminal double bond of the allene (Entry 7). Whereas, in the case of zero-valent platinum catalyst ($Pt(PPh_3)_4$), the thiolative carbonylation took place at the both terminal and central double bonds (Entry 6). Although $Pt(cod)Me_2$, which was expected to generate Pt(0) species in situ, could not catalyze this reaction, the addition of phosphine ligands gave **2a** and **3a**. This result suggests that Pt catalyst requires phosphine ligands (Entries 8 and 9).

Table 1. Transition-metal-catalyzed carbonylative thiolation



Entry	Catalyst	Solvent	Yield[a] (%)		
			2a	**3a** [*E*/*Z*]	Total
1	$Pd(PPh_3)_4$	Benzene	0	0	0
2	$Pd(OAc)_2$	THF	0	0	0
3	$RhCl(PPh_3)_3$	EtOH	0	0	0
4	$RhH(CO)(PPh_3)_3$	CH_3CN	0	0	0
5	$Co_2(CO)_8$	CH_3CN	0	0	0
6	$Pt(PPh_3)_4$	CH_3CN	39	48 [80/20]	87
7	$PtCl_2(PPh_3)_2$	CH_3CN	Trace	35 [85/15]	35
8[b]	$Pt(cod)Me_2$	CH_3CN	0	0	0
9[c]	$Pt(cod)Me_2$	CH_3CN	7	17 [77/23]	24
10[d]	None	CH_3CN	0	0	0

Reaction conditions: allene (3.8 mmol), thiol (0.5 mmol), CO (3 MPa), catalyst (15 mol %), solvent (1 mL), 120 °C, and 4 h.

[a] Determined by ^{1}H NMR.

[b] Allene (2 mmol), thiol (0.5 mmol), and catalyst (3 mol %).

[c] Allene (1.2 mmol), thiol (1.0 mmol), catalyst (3 mol %), and PPh_3 (9 mol %).

[d] Allene (2 mmol) and thiol (1.0 mmol).

Table 2. Influence of solvents for platinum(0)-catalyzed carbonylative thiolation

Entry	Solvent	Yield[a] (%)		
		2a	**3a** [*E*/*Z*]	Total
1	THF	12	14 [72/28]	26
2	Benzene	10	17 [72/28]	27
3	EtOH	3	3 [24/76]	6
4[b]	CH_3CN	39	48 [80/20]	87

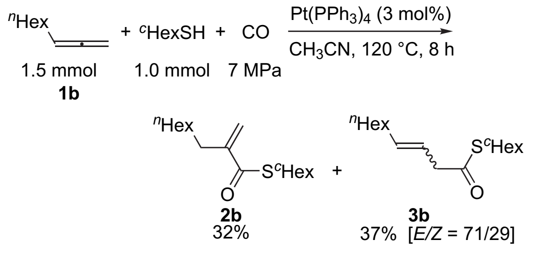
Reaction conditions: allene (2 mmol), thiol (0.5 mmol), CO (3 MPa), $Pt(PPh_3)_4$ (3 mol %), solvent (1 mL), 120 °C, and 4 h.

[a] Determined by ^{1}H NMR.

[b] Allene (3.8 mmol), thiol (0.5 mmol), and catalyst (15 mol %).

Table 2 summarizes the results of the platinum-catalyzed carbonylative thiolation of cyclohexylallene (**1a**) in various solvents. Ethereal solvent like THF, nonpolar solvent like benzene and protic solvent like EtOH were ineffective for the desired carbonylative thiolation (Entries 1–3). CH_3CN, which has both suitable polarity and coordinating property, worked as a good solvent (Entry 4).

The carbonylative thiolation of some other substituted allenes are shown in Eqs. 6–8. Monosubstituted allenes underwent the carbonylative thiolation to provide the corresponding α,β- and β,γ-unsaturated thioesters successfully (Eqs. 6 and 7). In the case of a cyclic allene, β,γ-unsaturated thioester (**3d**) was obtained preferentially (Eq. 8).



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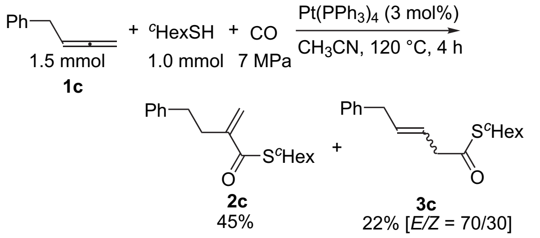

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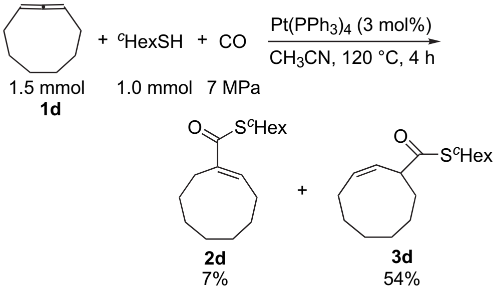
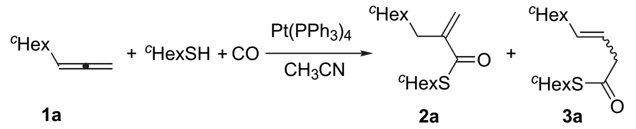


(8)

To get insight into the reaction pathway for this carbonylative thiolation, influence of the pressure of carbon monoxide on the product selectivity was studied. Interestingly, the ratios of **2a**/**3a** (i.e., the ratio of internal addition/terminal addition) were increased dramatically, with increase in the pressure of carbon monoxide (Table 3 and Fig. 1).

In the case of low pressure (1 MPa), β,γ-unsaturated thioester (**3a**) was obtained preferentially in 61% yield (Entry 1). Under 7 MPa of carbon monoxide, the yield of β,γ-unsaturated thioester (**3a**) was decreased to 22%, but the yield of α,β-unsaturated thioester (**2a**) was increased to 48% (Entry 4).

Table 3. Influence of carbon monoxide pressure for Pt(PPh$_3$)$_4$-catalyzed carbonylative thiolation



Entry	CO (MPa)	Yield[a] (%)		
		2a	**3a** [*E*/*Z*]	Total
1	1	30	61 [82/18]	91
2	3	39	48 [80/20]	87
3	5	44	33 [80/20]	77
4[b]	7	48	22 [80/20]	70
5[c]	7	50	24 [80/20]	74

Reaction conditions: allene (3.8 mmol), thiol (0.5 mmol), Pt(PPh$_3$)$_4$ (15 mol %), CH$_3$CN (1 mL), 120 °C, and 4 h.

[a] Determined by ^{1}H NMR.

[b] Pt(PPh$_3$)$_4$ (3 mol %) and allene (2.0 mmol).

[c] 8 h.

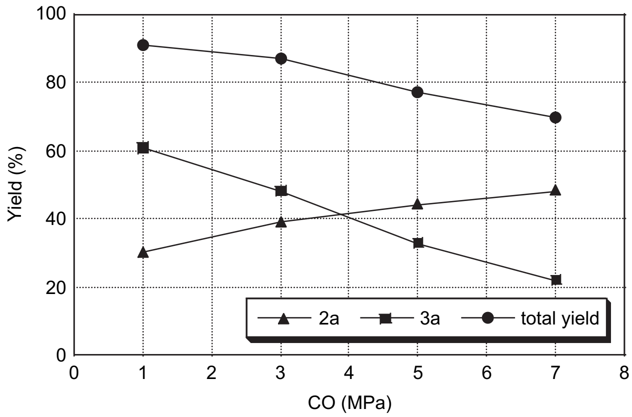
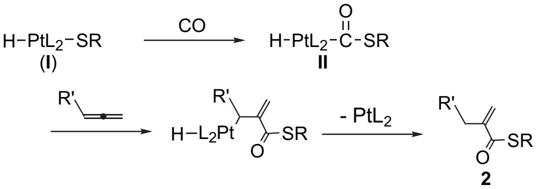


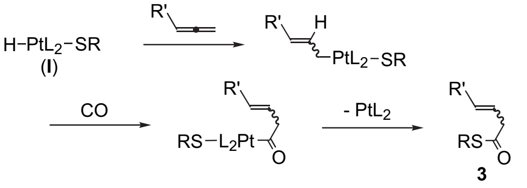
Figure 1. Influence of carbon monoxide pressure for Pt(PPh$_3$)$_4$-catalyzed carbonylative thiolation.

The high pressure of carbon monoxide resulted in the low total yield. Most probably, the coordination sites of platinum complex may be occupied by dissolved carbon monoxide to inhibit the following processes (Eqs. 9–11).

$$\mathrm{PtL_4} \xrightarrow{-2L} \mathrm{PtL_2} \xrightarrow{RSH} \underset{\mathbf{I}}{\mathrm{H{-}PtL_2{-}SR}} \qquad (9)$$



(10)



(11)

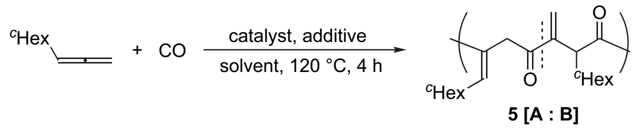
Eqs. 9–11 show possible pathways for this carbonylative thiolation: (1) oxidative addition of thiol (RSH) to Pt(PPh$_3$)$_4$ forms H–Pt–SR species (**I**) (Eq. 9); (2) coordination of carbon monoxide and subsequent insertion into the Pt–S bond takes place when the pressure of carbon monoxide is high; (3) coordination of allenes and subsequent acylplatination proceeds at the internal carbon–carbon double bond of the allene to give α,β-unsaturated thioester **2** after reductive elimination (Eq. 10). In the case of high pressure of CO, Pt undergoes coordination of CO to generate acylplatinum complex (**II**), the electron density of which is probably very low due to both the electron abstraction by the acyl groups and the back donation of CO ligands. Accordingly, acylplatination species (**II**) coordinate the relatively electron-rich double bonds (i.e., inner double bond of the allene). In contrast, when the pressure of carbon monoxide is low, coordination of allenes takes place prior to insertion of carbon monoxide. Probably, Pt still bears phosphine ligands, which act as electron-donating ligands and enhance the electron density on Pt. Thus, the hydroplatination takes place at the relatively electron-poor terminal carbon–carbon double bond of the allene, and then carbon monoxide insert into the Pt–C bond. Reductive elimination takes place sequentially to form β,γ-unsaturated thioester **3** (Eq. 11).[16,17]

2.2. Rhodium-catalyzed copolymerization of allenes and carbon monoxide

As mentioned in Table 1, RhCl(PPh$_3$)$_3$ in EtOH and RhH(CO)(PPh$_3$)$_3$ in CH$_3$CN did not exhibit catalytic activity toward the desired carbonylative thiolation (Table 1, Entries 3 and 4). Interestingly, however, the copolymerization product derived from cyclohexylallene and carbon monoxide was obtained as the major product (Table 4).

This polyketone is composed of the units **A** and **B** formed via the addition to the terminal double bond (**A**) and the internal double bond (**B**) of the allene, respectively.[18]

Table 4. Transition-metal-catalyzed copolymerization of allene with CO in the presence/absence of thiol or disulfide



5 [A : B]

Entry	Catalyst	Additive (mmol)	Solvent	Yield[a] (%)	[**A**:**B**]
1	$RhHCO(PPh_3)_3$	—	CH_3CN	85	[99:1]
2	$RhHCO(PPh_3)_3$	^{c}HexSH (0.5)	CH_3CN	89	[97:3]
3	$RhHCO(PPh_3)_3$	$(PhS)_2$ (0.5)	CH_3CN	92	[82:18]
4	$RhCl(PPh_3)_3$	—	EtOH	63	[95:5]
5	$RhCl(PPh_3)_3$	^{c}HexSH (0.5)	EtOH	43	[100:0]

Reaction conditions: catalyst (2.5–15 mol %), solvent (1 mL), allene (2.0–3.8 mmol), thiol (0.5 mmol), and CO (3 MPa).

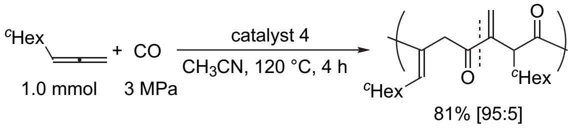
[a] Determined by ^{1}H NMR; based on allene employed.

In the presence of cyclohexanethiol, the $RhH(CO)(PPh_3)_3$-catalyzed copolymerization took place in high yield with good selectivity of unit **A/B** (Entry 2). In the absence of thiols, the yield of **5** was slightly low, but the ratios of **A/B** were increased. The molecular weight of the polymer is as follows: M_n=22,000; M_w/M_n=2.2 (Entry 1).

To explore the effect of the cyclohexanethiol on this copolymerization, the reaction of the $RhH(CO)(PPh_3)_3$ with cyclohexanethiol was examined. The reaction of the $RhH(CO)(PPh_3)_3$ (0.075 mmol) with cyclohexanethiol (0.5 mmol) at room temperature in CH_3CN (1 mL) under nitrogen atmosphere afforded a yellow solid (**4**) with the evolution of hydrogen (Eq. 12).[9a]

$$RhH(CO)(PPh_3)_3 + {}^cHexSH \xrightarrow{\text{r.t., 4 h}} \underset{\mathbf{4}}{Rh(S^cHex)(CO)(PPh_3)_3} + H_2 \quad (12)$$

The reaction of cyclohexylallene and carbon monoxide in the presence of complex **4** as a catalyst afforded the corresponding product **5** in good yield.



(13)

These results strongly suggest that rhodium thiolate complex exhibits a catalytic activity towards the copolymerization of allenes and carbon monoxide.

3. Conclusion

We have developed a highly selective carbonylation of allenes with carbon monoxide and thiols catalyzed by transition-metal catalysts. By the selection of the catalysts, carbonylative thiolation of allenes and copolymerization of allenes and carbon monoxide can take place selectively. These results mentioned in this paper suggest that novel combination of organic sulfur compounds and transition-metal catalysts is synthetically useful.

4. Experimental

4.1. General procedure for the $Pt(PPh_3)_4$-catalyzed carbonylative thiolation of allenes with carbon monoxide and thiols

In a 50 mL stainless steel autoclave with a magnetic stirring bar under nitrogen atmosphere were placed $Pt(PPh_3)_4$ (3–15 mol %), solvent (1 mL), allene (1.2–3.8 mmol), and thiol (0.5–1.0 mmol). Carbon monoxide was purged for three times and then charged at 3–7 MPa. The reaction was conducted with magnetic stirring for 4 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 a preparative TLC eluted by hexane/ethyl acetate (0:10 for Eq. 6; 4:1 for Eq. 7; 1:9 for Eq. 8) and/or a recycling preparative HPLC (Japan Analytical Industry, Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC) with $CHCl_3$ as eluent.

4.1.1. 2-(Cyclohexylthiocarbonyl)-3-cyclohexyl-1-propene (2a). A colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81–0.93 (m, 2H), 1.10–1.34 (m, 4H), 1.34–1.48 (m, 5H), 1.51–1.99 (m, 10H), 1.83–1.98 (m, 2H), 2.20 (d, J=6.6 Hz, 2H), 3.43–3.60 (m, 1H), 5.47 (s, 1H), 6.06 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 26.0, 26.2, 26.4, 33.0, 36.6, 39.9, 42.2, 122.8, 147.3, 194.0; IR (NaCl) 2926, 2853, 1661, 1624, 1448, 1263, 980, 928 cm^{-1}; HRMS calcd for $C_{16}H_{26}OS$: 266.1704. Found 266.1705; Anal. Calcd for $C_{16}H_{26}OS$: C, 72.12; H, 9.84; S, 12.03. Found: C, 72.09; H, 9.74; S, 11.91.

4.1.2. 2-(Cyclohexylthiocarbonyl)-1-nonane (2b). A colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80–0.93 (m, 3H), 1.20–1.34 (m, 11H), 1.34–1.52 (m, 3H), 1.51–1.80 (m, 4H), 1.83–2.01 (m, 2H), 2.30 (t, J=6.6 Hz, 2H), 3.40–3.60 (m, 1H), 5.49 (s, 1H), 6.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.1, 22.6, 25.6, 26.0, 28.2, 29.1, 29.2, 31.8, 33.1, 42.2, 121.5, 148.9, 193.9; IR (NaCl) 2928, 2855, 1661, 1625, 1448, 1263, 974, 930 cm^{-1}; HRMS calcd for $C_{16}H_{28}OS$: 268.1861. Found 268.1858; Anal. Calcd for $C_{16}H_{28}OS$: C, 71.58; H, 10.51; S, 11.94. Found: C, 71.32; H, 10.28; S, 11.29.

4.1.3. 2-(Cyclohexylthiocarbonyl)-4-phenyl-1-butene (2c). A colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21–1.34 (m, 1H), 1.37–1.53 (m, 4H), 1.53–1.66 (m, 1H), 1.66–1.80 (m, 2H), 1.85–2.02 (m, 2H), 2.58–2.68 (m, 2H), 2.72–2.81 (m, 2H), 3.47–3.64 (m, 1H), 5.47 (s, 1H), 6.06 (s, 1H), 7.14–7.23 (m, 3H), 7.24–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 26.0, 33.1, 33.8, 34.7, 42.3, 122.4, 126.0, 128.3, 128.5, 141.2, 147.8, 193.4; IR (NaCl) 3026, 2930, 2853, 1659, 1626, 1497, 1448, 1263, 999, 972, 930 cm^{-1}; Anal. Calcd for $C_{17}H_{22}OS$: C, 74.40; H, 8.08; S, 11.68. Found: C, 74.21; H, 8.24; S, 11.85.

4.1.4. Cyclohexyl 4-cyclohexyl-3-butenethioate (3a). Isolated as a mixture of (E-) and (Z-) isomers (73/27); a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97–1.20 (m, 3H), 1.20–1.36 (m, 8H), 1.36–1.51 (m, 6H), 1.52–1.80 (m, 2H), 1.83–2.04 (m, 2H), 3.17 (d, J=6.3 Hz, 1.64H, E-isomer), 3.27 (d, J=6.3 Hz, 0.41H, Z-isomer), 3.41–3.56 (m, 1H), 5.36–5.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 25.4, 25.7, 25.8, 26.0, 32.6, 32.8, 32.9, 36.5, 40.5, 42.1, 47.8, 118.7, 119.0, 140.5, 142.0, 198.5; IR (NaCl) 2926, 2851, 1682, 1448, 1263, 968, 887 cm^{-1}; HRMS calcd for $C_{16}H_{26}OS$: 266.1704. Found 266.1705; Anal. Calcd for $C_{16}H_{26}OS$: C, 72.12; H, 9.84; S, 12.03. Found: C, 71.85; H, 9.47; S, 11.94.

4.1.5. Cyclohexyl 3-decenethioate (3b). Isolated as a mixture of (*E*-) and (*Z*-) isomers (73/27); a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84–0.92 (m, 3H), 1.18–1.33 (m, 8H), 1.33–1.51 (m, 6H), 1.52–1.63 (m, 2H), 1.63–1.77 (m, 2H), 1.79–1.98 (m, 2H), 1.98–2.11 (m, 2H), 3.18 (d, *J*=6.3 Hz, 1.46H, *E*-isomer), 3.26 (d, *J*=6.3 Hz, 0.54H, *Z*-isomer), 3.43–3.56 (m, 1H), 5.42–5.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.5, 25.9, 28.7, 29.0, 31.7, 32.5, 33.0, 42.2, 42.7, 47.8, 120.5, 121.3, 134.7, 136.3, 198.1; IR (NaCl) 2928, 2855, 1690, 1448, 1263, 997, 966, 887 cm^{-1}; HRMS calcd for $C_{16}H_{28}OS$: 268.1861. Found 268.1855; Anal. Calcd for $C_{16}H_{28}OS$: C, 71.58; H, 10.51; S, 11.94. Found: C, 71.51; H, 10.30; S, 11.67.

4.1.6. Cyclohexyl 5-phenyl-3-pentenethioate (3c). Isolated as a mixture of (*E*-) and (*Z*-) isomers. It is difficult to determine the ratio of *E*/*Z* based on ^{1}H NMR. The ratio of *E*/*Z* is determined tentatively by^{13}C NMR as 70/30; a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20–1.33 (m, 1H), 1.33–1.51 (m, 4H), 1.51–1.63 (m, 1H), 1.63–1.80 (m, 2H), 1.85–2.0 (m, 2H), 3.23 (d, *J*=6.8 Hz, 2H), 3.39 (d, *J*=6.3 Hz, 1.4H, *E*-isomer), 3.44 (d, *J*=7.3 Hz, 0.6H, *Z*-isomer), 3.46–3.57 (m, 1H), 5.56–5.68 (m, 1H), 5.68–5.85 (m, 2H), 7.11–7.24 (m, 3H), 7.24–7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 26.0, 33.0, 33.7, 38.9, 42.3, 42.7, 47.6, 121.6, 123.0, 126.1, 128.4, 128.5, 128.6, 132.6, 134.3, 140.0, 197.7; IR (NaCl) 3026, 2930, 2853, 1688, 1494, 1450, 1263, 997, 970 cm^{-1}; HRMS calcd for $C_{17}H_{22}OS$: 274.1391. Found 274.1395.

4.1.7. Cyclohexyl 1-cyclononene-1-carbothiolate (2d) and cyclohexyl 2-cyclononene-1-carbothiolate (3d). Isolated as a mixture of α,β- and β,γ-isomers. The ratio of **2d**/**3d** isomer was determined by ^{1}H NMR as 10/90; a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06–1.79 (m, 18H), 1.79–2.05 (m, 2H), 2.05–2.53 (m, 2H), 3.42–3.57 (m, 1H), 3.63 (ddd, *J*=3.3, 10.2 Hz, 0.9H, **3d**), 5.52 (t, *J*=10.2 Hz, 0.9H, **3d**), 5.72 (ddd, *J*=2.4, 7.5, 8.1 Hz, 0.9H, **3d**), 6.84 (t, *J*=8.7 Hz, 0.1H, **2d**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0, 25.1, 25.3, 25.3, 25.6, 25.7, 25.9, 26.1, 26.3, 26.6, 30.4, 30.6, 33.1, 33.3, 37.7, 38.0, 42.1, 52.2, 127.6 (**3d**), 131.9 (**3d**), 140.5 (**2d**), 154.5 (**2d**), 193.8 (**2d**), 201.6 (**3d**); IR (NaCl) 3014, 2927, 2852, 1693, 1682, 1651, 1446, 1346, 1263, 999 cm^{-1}; HRMS calcd for $C_{16}H_{26}OS$: 266.1704. Found 266.1705; Anal. Calcd for $C_{16}H_{26}OS$: C, 72.12; H, 9.84; S, 12.03. Found: C, 72.11; H, 9.56; S, 11.82.

4.2. General procedure for the rhodium-catalyzed copolymerization of allenes and carbon monoxide

In a 50 mL stainless steel autoclave with a magnetic stirring bar under nitrogen atmosphere were placed Rh catalyst (3–15 mol %), solvent (1 mL), allene (2.0–3.8 mmol), and thiol or disulfide (0.5 mmol). Carbon monoxide was purged for three times and then charged at 3 MPa. The reaction was conducted with magnetic stirring for 4 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 reprecipitation ($CHCl_3$/MeOH). The polymers were characterized by NMR spectroscopy, IR, and GPC measurements (polystyrene standards, eluent: THF).

4.2.1. Polyketone 5. A pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95–1.20 (m, 3H), 1.20–1.41 (m, 2H), 1.45–1.85 (m, 6H), 2.11–2.34 (m, 1H), 3.67 (s, 2H), 5.45 (d, *J*=6.0 Hz, unit B $=CH_2$), 6.64 (d, *J*=9.8 Hz, unit A $=CH$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 31.9, 34.6, 38.2, 134.0, 149.9, 198.9. Other signals of the minor structural unit (unit B) are not assigned unambiguously. IR (NaCl) 2924, 2851, 1738, 1668, 1448, 1373, 1317, 1240, 1124, 1028, 972, 901, 842 cm^{-1}.

Acknowledgements

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16. In this reaction, reductive elimination selectively takes place after insertion of CO. Indeed, the formation of allylic sulfides (derived from allylic platinum species by the reductive elimination) was not detected at all.
17. This platinum-catalyzed carbonylative thiolation involves two key platinum species, i.e., H–Pt–SR (I) and H–Pt–C(O)SR (II). Allenes may insert preferentially into Pt–X bonds (X=H, SR, and C(O)SR) by the order of Pt–C(O)SR>H–Pt>Pt–SR, although the real reason to explain this tendency should wait for further detailed mechanistic study. On the other hand, the regioselectivity of the catalysis suggests terminal attachment of the bulkier platinum moiety at the insertion stage. Also, the stability between allylic platinum species (formed by terminal attack) and vinylic platinum species (formed by inner attack) may contribute to the reaction course. Cf., (a) 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; (b) Hirai, T.; Kuniyasu, H.; Kambe, N. *Chem. Lett.* **2004**, *33*, 1148; (c) Hirai, T.; Kuniyasu, H.; Kambe, N. *Tetrahedron Lett.* **2005**, *46*, 117.
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