Palladium-Catalyzed Azathiolation of Carbon Monoxide

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A novel palladium-catalyzed azathiolation of carbon monoxide using sulfenamide ($RSNR'_2$) (**1**) is described to provide thiocarbamate **2** in good yields. The mechanistic proposal includes the following: (1) insertion of CO into Pd−S bond of $Pd(SR)_2(PPh_3)_n$ **4** to provide $Pd[C(O)SR](SR)(PPh_3)_n$ **5** and (2) σ-bond metathesis between S−N and Pd−C(O) bonds to afford **2** with the regeneration of **4**.

Introduction

A variety of transition-metal-catalyzed reactions of Y−G (Y = S, Se) bond compounds with unsaturated compounds such as acetylenes and CO have been developed lately, in which the polarity of Y−G is $Y^{\delta-}-G^{\delta+}$ (G = H,[1,2] Si,[3] Ge,[3] B,[4] and P[5]) or neutral (G = S,[6] Se[6]). These have served as a useful strategy in organic synthesis and stimulated further study to uncover the hidden reactivity of chalcogenates on metals.[7] Herein described is a novel metal-catalyzed *azathiolation of carbon monoxide* using sulfenamide ($RSNR'_2$) (**1**) whose unique $S^{\delta+}-N^{\delta-}$ bond character is a stereoelectronic component of the reaction.[8,9]

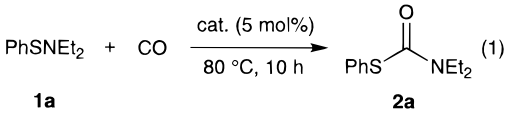
Results and Discussion

We have found that the reaction of *S*-phenyl-*N*-diethylsulfenamide $PhSNEt_2$ (**1a**) (1 mmol) with CO (20 kg/cm^2) was catalyzed by 5 mol % of $Pd(PPh_3)_4$ in pyridine (0.5 mL) at 80 °C for 10 h to provide *N*-diethyl phenylthiocarbamate **2a** in 90% yield (eq 1, run 1 of Table 1).

Table 1. Effects of Catalyst and Solvent on the Reaction of 1a with CO[a]

run	catalyst	solvent	yield[b] (%)
1	$Pd(PPh_3)_4$	pyridine	90[c]
2	$Pd_2(dba)_3$	pyridine	29
3	$Rh(PPh_3)_3Cl$	pyridine	67[c]
4	$Pd(PPh_3)_4$	none	3
5	$Pd(PPh_3)_4$	C_6H_6	6
6	$Pd(PPh_3)_4$	C_6H_6[d]	11
7	$Pd(PPh_3)_4$	C_6H_6[e]	48

[a] **1a** (1 mmol), CO (20 kg/cm^2), and solvent (0.5 mL). [b] NMR yield. [c] Isolated yield. [d] With 0.05 mmol of pyridine. [e] With 1 mmol of pyridine.



The formation of 3% of Et_2NH and 1.4% of $[Et_2NC(O)]_2$ was also confirmed by the ^1H NMR spectrum of the crude reaction mixture. The reaction was also catalyzed by $Pd_2(dba)_3$ (29%) and $Rh(PPh_3)_3Cl$ (67%) in pyridine (runs 2 and 3). Reactions performed in benzene, CH_3CN, DMSO, HMPA, Et_3N, and *N*-methylmorpholine or without solvent only ended in producing a poor yield of **2a** (runs 4 and 5 as examples). Pyridine was indispensable as a solvent for completion of the reaction under the conditions employed (runs 6 and 7). Among the catalysts examined, $Pt(PPh_3)_4$, $Ni(PPh_3)_2Cl_2$, $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$, and $W(CO)_6$ were hardly active even in pyridine.

The result of the reactions of some sulfenamides with CO was summarized in Table 2. The reaction using *p*-$tolSNEt_2$ (**1b**) was not completed in 10 h (run 1), but was after 20 h to afford 86% of **2b** (run 2). On the other hand, *p*-$ClC_6H_4SNEt_2$ (**1c**), *p*-$FC_6H_4SNEt_2$ (**1d**), and *m*-$MeOC_6H_4SNEt_2$ (**1e**) reacted faster than **1a** to give good yields of **2** (5 h for **2c** (85%) and **2d** (84%); 3 h for **2e** (81%), runs 3−5). Replacement of ArS by benzyl-S^- (**1f**) and BuS^- (**1g**) retarded carbonylation; more severe reaction conditions (100 °C, 20 h) were required to provide 26% and 43% of thiocarbamate, respectively (runs 6 and 7). The reactions using $ArSNMe_2$ proceeded faster than that of $ArSNEt_2$, and were completed within

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(9) Electronegativity (Pauling): S, 2.5; Se, 2.4; H, 2.1; Si, 1.8; Ge, 1.8; B, 2.0; P, 2.1; N, 3.0.

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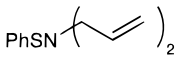
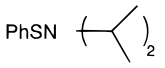
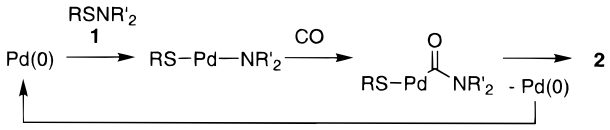
Table 2. Palladium-Catalyzed Azathiolation of CO[a]

run	1		time (h)	2	yield (%)[b]
	$ArSNEt_2$				
1	Ar = *p*-tol	**1b**	10	**2b**	62[c,d]
2		**1b**	20		86
3	Ar = *p*-ClC_4H_6	**1c**	5	**2c**	85
4	Ar = *p*-FC_4H_6	**1d**	5	**2d**	84
5	Ar = *m*-$MeOC_4H_6$	**1e**	3	**2e**	81
6	$PhCH_2SNEt_2$	**1f**	20[e]	**2f**	26
7	$BuSNEt_2$	**1g**	20[e]	**2g**	43
	$ArSNMe_2$				
8	Ar = Ph	**1h**	3	**2h**	90
9	Ar = *p*-ClC_4H_6	**1i**	2	**2i**	83
10	PhSN(H)Et	**1j**	1		-[f]
11		**1j**	15 min		-[g]
12		**1k**	20	**2k**	83
13		**1l**	20[e]	**2l**	0
14	PhSN(H)Ph	**1m**	20[e]	**2m**	0

[a] **1** (1 mmol), CO (20 kg/cm^2), and $Pd(PPh_3)_4$ (0.05 mmol) in pyridine (0.5 mL) at 80 °C. Reaction times were roughly optimized. [b] Isolated yield. [c] NMR yield. [d] 29% of **1b** was recovered. [e] 100 °C. [f] Et(H)NC(O)N(H)Et (**3**) (85%) and $(PhS)_2$ (84%) were obtained. [g] 30% of **3** was obtained.

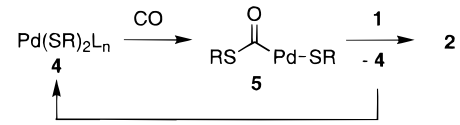
Scheme 1. An Unlikely Path of Pd-Catalyzed Azathiolation of CO



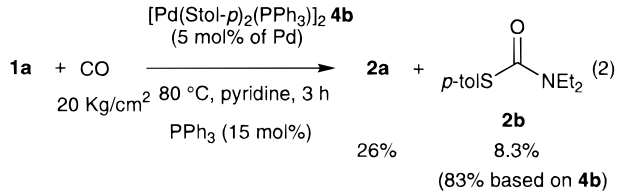
3 h (compare run 1 in Table 1 with run 8, and run 3 with run 9). When the reaction of PhSN(H)Et (**1j**) with CO was carried out, 85% of Et(H)NC(O)N(H)Et **3** and 84% of $(PhS)_2$ were obtained after 1 h (run 10). No formation of PhSC(O)N(H)Et (**2j**) was confirmed, even if the reaction was stopped after 15 min (30% of **3**) (run 11), indicating that **2j** formed in situ was very susceptible to the nucleophilic substitution by **1j** to afford **3** and $(PhS)_2$. While $PhSN(allyl)_2$ (**1k**) reacted with CO to furnish 83% of **2k** after 20 h (run 12), the reactions employing more hindered $PhSN(Pr\text{-}i)_2$ (**1l**) or PhSN(H)Ph (**1m**) did not take place even at 100 °C (runs 13 and 14).

With regard to the reaction mechanism of the present Pd-catalyzed azathiolation of CO, a path involving oxidative addition of **1** to Pd(0), insertion of CO into Pd−N bond,[10,11] and subsequent reductive elimination can be envisioned (Scheme 1). However, this path is unlikely judging from the following observations. (1) The ^{31}P NMR spectrum of crude reaction mixture of $Pd(PPh_3)_4$-catalyzed reaction of **1a** with CO showed the formation of $[Pd(SPh)_2(PPh_3)]_2$ **4a**[12] in 56% yield after 3 h and 59% yield after 10 h. (2) **4a** was actually active as a catalyst under the carbonylation of **1a** to form **2a** in 30% (5 mol % of Pd, 80 °C, 10 h) or even 84% yield if 15 mol % of PPh_3 was added. (3) No formation of imine, which can be generated from Pd−NR′$_2$, was confirmed under the reactions performed in Tables 1 and 2.[13] (4) No reaction was observed in the stoichiometric reaction of **1a** with $Pd(PPh_3)_4$ even at 80 °C for 12 h.

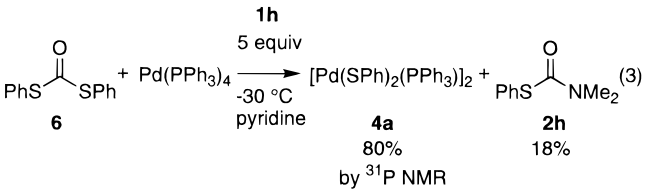
Scheme 2. Proposed Propagation of Pd-Catalyzed Azathiolation of CO



An alternative propagation shown in Scheme 2 involves an insertion of CO into the Pd−S bond of **4** to provide Pd[C(O)SR](SR) **5**[14] followed by reaction with **1** to give **2** with regeneration of **4** (Scheme 2). According to this mechanism, the RS group in **4** and the R′$_2$N group of **1** are incorporated into newly forming **2**. Indeed, when $[Pd(Stol\text{-}p)_2(PPh_3)]_2$ **4b** was used as a catalyst in the reaction of $PhSNEt_2$ **1a** with CO, 83% of *p*-tolS of **4b** was converted into **2b** at the beginning stage of the reaction (eq 2). (Note that the carbonylation of **1b** was slower than that of **1a**.) Although we were not able to confirm the



formation of **5** even by the reaction of **4** with CO,[15] the reactivity of **5** with **1** in Scheme 2 was examined as follows. When 1 equiv of PhSC(O)SPh **6** was added into the pyridine solution of $Pd(PPh_3)_4$ in the presence of 5 equiv of **1h** at −30 °C over 10 min, the formation of 80% of **4a** was confirmed by ^{31}P NMR and 18% of **2h** was isolated by preparative TLC (eq 3).[16] This fact clearly



indicated that some of short-lived Pd[C(O)SPh](SPh)-$(PPh_3)_n$ **5a** generated by the oxidative addition of **6** to Pd(0) was actually intercepted by **1h** before deinsertion of CO from **5a** took place. A proposed transition state **7** in the reaction of **5** with **1** was shown in Scheme 3, in which RS−NR′$_2$ simultaneously interacted with both Pd and electrophilic RSC(O) to provide the driving force of

(10) Alper et al. have reported the Co-catalyzed carbonylation of thiazolidines, in which insertion of CO into the Co−N bond has been proposed. See: Khumtaveeporn, K.; Alper, H. *J. Am. Chem. Soc.* **1994**, *116*, 5662.

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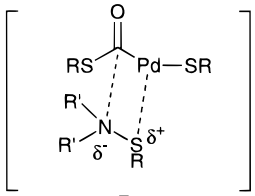
Scheme 3. Proposed Transition State



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the reaction.[17] This process, facilitated by the electron-withdrawing substituent in RSC(O) and suppressed by the bulky group in R'_2N, would determine the whole reaction rate of Pd-catalyzed carbonylation of **1**.

In conclusion, this paper reported a novel azathiolation of carbon monoxide, demonstrating the efficiency of the S−N bond compound as a substrate in transition-metal-catalyzed reactions. Further study to develop a new transformation using sulfenamide is currently underway.

Experimental Section

General Methods. ^{1}H, ^{13}C, and ^{31}P NMR spectra in $CDCl_3$ and benzene-d_6 solution were recorded with a JEOL JNM-GSX-270 (270 MHz) spectrometer. The chemical shifts in the ^{1}H and ^{13}C NMR spectra were recorded relative to Me_4Si (or C_6H_6 δ 7.16) and $CDCl_3$ (δ 77.0), respectively. ^{31}P NMR spectra were recorded using 85% H_3PO_4 as an external standard. IR spectra were recorded with a Perkin-Elmer model 1600 spectrometer. Combustion analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. The synthesis and purification of substrates, catalysts, and solvents are described in the Supporting Information. Preparative TLC was carried out using Wakogel B-5F silica gel.

Palladium-Catalyzed Azathiolation of Carbon Monoxide: General Procedure (Eq 1, Table 1). Preparation of $PhSC(O)NEt_2$ (2a). Into a 50-mL stainless steel autoclave were added *S*-phenyl-*N*-diethylsulfenamide **1a** (181 mg, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and pyridine (0.5 mL). Then the mixture was heated at 80 °C for 10 h under 20 kg/cm^2 of carbon monoxide with magnetic stirring. The ^{1}H NMR spectrum of the crude homogeneous reaction mixture taken in benzene-d_6 showed the formation of **2a**, 3% of Et_2NH, and 1.4% of $Et_2NC(O)C(O)NEt_2$. The yield was determined from the relative ratio of **2a**, Et_2NH, and $[Et_2NC(O)]_2$. The ^{31}P NMR spectrum showed the formation of $[Pd(SPh)_2(PPh_3)]_2$ **4a** in 59% yield (calculated based on all signals observed). The signals of Et_2NH, $[Et_2NC(O)]_2$, and **3a** were assigned by the comparison with those of authentic samples. Then ca. 50 mL of hexane/Et_2O (1/1) was added into the crude reaction mixture, the brown precipitate was removed through Celite, the residual filtrate was concentrated in vacuo, and the residual mixture was purified by PTLC using Et_2O/hexane (3/7) as an eluent. A 188 mg (90%) of *S*-phenyl *N*-diethyl thiocarbamate **2a** was isolated as a clear colorless oil. Reactions listed in Table 2 were carried out similarly. The reaction times in Table 2 were roughly optimized (1, 2, 3, 5, 10, or 20 h). The NMR yields in Tables 1 and 2 were determined from the crude reaction mixture based on the relative ratio of **1**, **2**, Et_2NH. The substrates, catalysts, solvent, and yields of **2** were listed in Tables 1 and 2.

2a: colorless oil; 188 mg, 90%; registry no. of **2a** (provided by the author): 51861-23-5.

***p*-tol-SC(O)NEt$_2$ (2b) (run 2 in Table 2):** colorless oil; 191 mg, 86%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.22 (br, 6 H), 2.35 (s, 3 H), 3.42 (q, J = 7.3 Hz, 4 H), 7.18 (d, J = 7.8 Hz, 2 H) 7.38 (d, J = 7.8 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.69, 21.26, 42.45, 125.19, 129.65, 135.69, 139.16, 166.04; IR (NaCl) 2975, 1667, 1404, 1248, 1219, 1115, 1094, 808 cm^{-1}; mass spectrum (EI) *m/e* 223 (M$^+$, 5). Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.54; H, 7.67; N, 6.27; S, 14.36. Found: C, 64.48; H, 7.62, N, 6.46; S, 14.11.

***p*-Cl-C$_6$H$_4$SC(O)NEt$_2$ (2c) (run 3 in Table 2):** colorless oil; 206 mg, 85%; registry no. of **2c** (provided by the author): 51861-26-8.

***p*-F-C$_6$H$_4$SC(O)NEt$_2$ (2d) (run 4 in Table 2):** colorless oil; 191 mg, 84%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.24 (br, 6 H), 3.41 (q, J = 7.0 Hz, 4 H), 7.06 (t, J = 7.8 Hz, J_{H-F} = 7.8 Hz, 2 H), 7.47 (dd, J = 7.8 Hz, J_{H-F} = 5.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.45 (br), 42.27, 42.37, 115.88 (d, J_{C-F} = 22.8 Hz), 124.06 (d, J_{C-F} = 2.7 Hz), 137.45 (d, J_{C-F} = 8.1 Hz), 161.42, 165.25 (d, J_{C-F} = 18.8 Hz); IR (NaCl) 2977, 1665, 1590, 1491, 1248, 1219, 1117, 831 cm^{-1}; mass spectrum (EI) *m/e* 227 (M$^+$, 5). Anal. Calcd for $C_{11}H_{14}FNOS$: C, 6.21; H, 6.16; N, 6.16. Found: C, 6.19; H, 6.19, N, 6.35.

***m*-MeOC$_6$H$_4$SC(O)NEt$_2$ (2e) (run 5 in Table 2):** colorless oil; 195 mg, 81%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.21 (br, 6 H), 3.42 (q, J = 7.0 Hz, 4 H), 3.80 (s, 3 H), 6.92 (dd, J = 5.9 Hz, 2.4 Hz, 1 H), 7.06−7.11 (m, 2 H), 7.29 (t, J = 8.1 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.29 (br), 42.23, 55.16, 55.24, 115.22, 120.57, 127.94, 129.45, 129.57, 159.46, 165.45; IR (NaCl) 2975, 1655, 1591, 1478, 1465, 1248, 1115, 853 cm^{-1}; mass spectrum (EI) *m/e* 239 (M$^+$, 13). Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85; S, 13.40. Found: C, 60.29; H, 7.28; N, 5.86; S, 13.37.

PhSCH$_2$C(O)NEt$_2$ (2f) (run 6 in Table 2): white solid; mp 30 °C; 57 mg, 26%; registry no. of **2f** (provided by the author): 30085-50-8.

BuSC(O)NEt$_2$ (2g) (run 7 in Table 2): colorless oil; 81 mg, 43%; registry no. of **2g** (provided by the author): 91852-97-0.

PhSC(O)NMe$_2$ (2h) (run 8 in Table 2): colorless solid, mp 30 °C; 163 mg, 90%; registry no. of **2h** (provided by the author): 7304-68−9.

***p*-ClC$_6$H$_4$SC(O)NMe$_2$ (2i) (run 9 in Table 2):** colorless solid; mp 78 °C; 179 mg, 83%; registry no. of **2i** (provided by the author): 7304-69-0.

Pd-Catalyzed Reaction of PhSN(H)Et (1j) with CO (Runs 10 and 11 in Table 2). A 91 mg (84%) of $(PhS)_2$ and a 49 mg (85%) of Et(H)NC(O)N(H)Et (**3**) were isolated by preparative TLC (80 °C, 1 h). When the reaction was carried out at 80 °C for 15 min, the formation of 30% (relative to unreacted **1j**) of **3** was confirmed by the ^{1}H NMR spectrum of the crude reaction; however, no formation of PhSC(O)N(H)Et (**2j**) was observed: mass spectrum of **3** (CI) *m/e* 171 (M + 1$^+$, 100).

PhSC(O)N(allyl)$_2$ (2k) (run 12 in Table 2): colorless oil; 194 mg, 83%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.01 (d, J = 5.9 Hz, 4 H), 5.24 (br, 4 H), 5.81 (br, 2 H), 7.38 (m, 3 H), 7.51 (m, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 39.45, 117.97, 128.43, 128.88, 129.13, 132.34, 135.19, 166.82; IR (NaCl) 1668, 1441, 1393, 1206, 980, 927, 750, 689 cm^{-1}; mass spectrum (EI) *m/e* 233 (M$^+$, 5). Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.48; N, 6.00; S, 13.74. Found: C, 66.81; H, 6.48; N, 6.09; S, 13.53.

Attempted Pd-Catalyzed Reaction of PhSN(Pr-*i*)$_2$ (1l) or PhSN(H)Ph (1m) with CO (Runs 13 and 14). The reaction of **1l** with CO (20 kg/cm^2) in the presence of 5 mol %

(14) The definitive evidences of insertion of CO into the M−S bond have been very rare. (a) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (b) Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 2609. (c) Shim, S. C.; Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 1935. (d) Takahashi, H.; Ohe, K.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *334*, C43. (e) Wang, M. D.; Calet, S.; Alper, H. *J. Org. Chem.* **1989**, *54*, 20. (f) Kim, Y. J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (g) Liu, H.; Tan, A. L.; Mok, K. F.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4023. (h) Luh, T. Y.; Ni, Z. J. *Synthesis* **1990**, 89. (i) Matsunaga, P. T.; Hillhouse, G. L. *Angew. Chem., Int. Engl.* **1994**, *33*, 1748. (j) Khumtaveeporn, K.; Alper, H. *J. Org. Chem.* **1994**, *59*, 1414. See also ref 1g and 6b.

(15) We have recently reported that the insertions of isocyanide into Pd−S bond of **4** was reversible and its equilibrium leaned to the deinsertion direction; see: Kuniyasu, H.; Sugoh, K.; Moon, S.; Kurosawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4669.

(16) The reaction of **1h** with **6** providing **2h** without $Pd(PPh_3)_4$ was very sluggish (2% after 12 h at rt).

(17) A bond metathesis between S−B and Pd−C bonds has been recently reported; see: Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 1383.

of $Pd(PPh_3)_4$ at 100 °C for 20 h did not provide any thiocarbamate. Only the formation of 28% of $(i\text{-Pr})_2NH$ was confirmed. The reaction using **1m** under the same reaction conditions gave 75% of $PhNH_2$ and 80% of $(PhS)_2$.

Attempted Oxidative Addition of 1a to $Pd(PPh_3)_4$. Into a two-necked glass flask equipped with a reflux condenser and a magnetic stirring bar were placed $Pd(PPh_3)_4$ (1.16 g, 1.0 mmol), **1a** (217 mg, 1.2 mmol), and pyridine (3.0 mL). After the mixture was heated at 80 °C for 12 h with magnetic stirring, the ^1H NMR spectrum of the crude the reaction mixture was taken. However, **1a** remained unreacted.

Confirmation of Resting State of Catalyst. Into a 50-mL stainless steel autoclave were added **1a** (181 mg, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and pyridine (0.5 mL). Then the mixture was heated at 80 °C for 3 h under 20 kg/cm^2 of carbon monoxide with magnetic stirring. The ^{31}P NMR spectrum of the crude homogeneous reaction mixture taken in benzene-d_6 showed the formation of 56% of **4a** (δ 31.75 and δ 33.10 in a ratio of 55/45).

Reaction of 1a with CO with $[Pd(Stol\text{-}p)_2(PPh_3)]_2$ (4b) as a Catalyst (Eq 2). After the reaction of **1a** (181 mg, 1.0 mmol) with CO (20 kg/cm^2) was carried out at 80 °C for 3 h in the presence of **4b** (30.8 mg, 0.025 mmol), the reaction mixture was subjected to preparative TLC. A 72 mg of mixture of **2a** (26%) and **2b** (8.3%) was obtained. The ratio of **2a** and **2b** was determined by the ^1H NMR spectrum.

The Stoichiometric Reaction of PhSC(O)SPh (6) with $Pd(PPh_3)_4$ in the Presence of 1h (Eq 3). In a dry 10 mL two-necked flask with 10 mL dropping funnel were placed $Pd(PPh_3)_4$ (120 mg, 0.104 mmol), **1h** (78 mg, 0.51 mmol), and pyridine (3 mL). Then the reaction mixture was cooled at −30 °C, and **6** (25 mg, 0.1 mL) dissolved in 3 mL of pyridine (3 mL) was added over 10 min. The ^{31}P NMR spectrum of the crude reaction mixture taken in benzene-d_6 after stirring for 1 h showed the formation of 80% of **4a**. Then ca. 50 mL of hexane was added, the precipitation was removed through Celite, and the filtrate was concentrated in vacuo. The residual reaction mixture was subjected to preparative TLC to afford 3.3 mg (18% based on **6**) of **2h**.

The Reaction of 6 with 1h (Ref 16). Into a dry NMR tube were placed **6** (25 mg, 0.1 mmol), **1h** (16 mg, 0.1 mmol), and pyridine-d_5 (0.5 mL). No reaction was confirmed at room temperature after 1 h by ^1H NMR spectrum. The formation of 2% of **2h** was confirmed after 12 h.

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Supporting Information Available: Listing of experimental procedures and analysis data for the compounds in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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