

## A Prototype of Transition-Metal-Catalyzed Carbothiolation of Alkynes

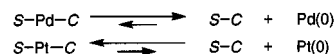
Kunihiko Sugoh, Hitoshi Kuniyasu,\* Taeko Sugae, Atsushi Ohtaka, Yasutomo Takai, Aoi Tanaka, Chikako Machino, Nobuaki Kambe,\* and Hideo Kurosawa\*

Department of Applied Chemistry, Faculty of Engineering  
Osaka University, Suita, Osaka 565-0871, Japan

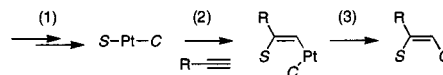
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The organic sulfides, which once had been considered to be catalyst poison,<sup>1</sup> have been proved to be versatile reagents for a variety of transition-metal-catalyzed reactions.<sup>2–5</sup> These transformations offered unique methodologies to build up desired organic compounds and clearly revealed the high reactivities of thiolate ligands on transition metals. The Pd-catalyzed decarbonylation of thioester R<sup>1</sup>SC(O)R<sup>2</sup> (**1**) (R<sup>1</sup> = aryl or alkyl; R<sup>2</sup> = aryl or vinyl)<sup>3</sup> and cross-coupling reactions of R<sup>1</sup>SM (**2**) (M: typical metal) with R<sup>2</sup>X (**3**) (X: halogen or OTf),<sup>4</sup> both furnishing R<sup>1</sup>SR<sup>2</sup> (**4**), are among the typical examples. It was also reported that the Pd-catalyzed addition of diaryl disulfide (ArS)<sub>2</sub> (**5**) to terminal alkyne R<sup>3</sup>CCH (**6**) gave vinyl sulfide (Z)-R<sup>3</sup>(ArS)C=CH(SAr) (**7**).<sup>5k</sup> These reactions indicated that facile S–C bond-forming reductive elimination (RE) from Pd(II) occurred to complete the catalytic cycles.<sup>6</sup> In marked contrast, we have recently found that the stoichiometric S–C bond-cleaving oxidative addition (OA) of vinyl sulfide **7** (R<sup>3</sup> = aryl, SiMe<sub>3</sub>, CH<sub>2</sub>-OMe) to Pt<sup>0</sup>L<sub>n</sub> afforded *cis*-Pt[(Z)-CH=C(SAr)(R<sup>3</sup>)](SAr)L<sub>n</sub> (**8**),<sup>7</sup> suggesting that the S–C bond-forming RE could be suppressed by simply switching metals from Pd to Pt in the above catalyses (Scheme 1).<sup>8,9</sup> Disclosed herein is a novel method for regio- and stereoselective additions of carbon and sulfur functionalities to alkynes based on the following working hypothesis: (1) S–Pt–C unit formation patterned after the Pd-catalyzed reactions, (2)

**Scheme 1.** General Trend of RE and OA of the S–C Bond from/to Pd and Pt Complexes



**Scheme 2.** Schematic Strategy for Carbothiolation of Alkyne



conversion into C–Pt–C by the insertion (IS) of alkyne into the S–Pt bond,<sup>5i,j</sup> and (3) subsequent C–C bond-forming RE<sup>10</sup> (Scheme 2).

It became evident that the reaction of PhSC(O)Ph (**1a**) (1.0 mmol) with 1-octyne (**6a**) (1.2 mmol) carried out in the presence of Pt(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol) under toluene (0.5 mL) reflux for 10 h indeed produced the anticipated (*Z*)-2-(phenylthio)-1-phenyl-1-octene (**9a**) in 77% yield (eq 1, run 1 of Table 1).<sup>11</sup> Neither isomers of **9a** nor PhSPh (**4a**) was detected.<sup>12</sup> When the reaction of **1a** with **6a** was performed with Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst,<sup>3</sup> **4a** was formed in 40% yield; however, no formation of **9a** was confirmed (run 2).<sup>13</sup> The functional groups such as *p*-Me (**1b**), *p*-Br (**1c**), and *p*-NO<sub>2</sub> (**1d**) on aromatic rings of R<sup>1</sup> did not adversely interfere with the reactions (runs 3–5). The reactions of BuSC(O)Ph (**1e**) or PhCH<sub>2</sub>SC(O)Ph (**1f**) with **6a** were very sluggish to give 33% and 46% of adducts (**9e** or **9f**) under xylenes reflux for 46 h, respectively (runs 6–9). The platinum-catalyzed arylthiolation of alkynes was not so sensitive to the electronic effect on the aromatic rings in R<sup>2</sup>; i.e., 74% of **9g** (*p*-Me) and 79% of **9h** (*p*-CN) were isolated (runs 10 and 11). The group R<sup>2</sup> can be replaced by a vinyl group to afford the vinylthiolation product **9i** in 63% yield with the stereochemistry of vinyl moiety retained (run 12). On the other hand, PhSC(O)Me (**1j**) was inert (run 13), while the reaction with PhSC(O)C<sub>8</sub>H<sub>17-n</sub> (**1k**) produced hydrothiolation product,<sup>5c,i</sup> 2-phenylthio-1-octene in 73% yield (run 14). Terminal alkynes such as 6-hydroxy-1-hexyne (**6b**), 5-cyano-1-pentyne (**6c**), phenyl acetylene (**6d**), and (trimethylsilyl)acetylene (**6e**) all underwent the carbothiolation by **1c** to furnish the corresponding adducts (**9l–9o**) in moderate yields (runs 15–18). The carbothiolation proceeded at both of the C–C triple bonds smoothly when 1,7-octadiyne (**6f**) was employed (run 19).

Then to get the convincing information on the mechanism of Pt-catalyzed carbothiolation of alkynes by thioester, some stoichiometric reactions were monitored by <sup>31</sup>P NMR spectra as follows. The OA of **1c** (0.02 mmol) to Pt(PPh<sub>3</sub>)<sub>4</sub> (0.01 mmol) in C<sub>6</sub>D<sub>6</sub> (0.6 mL) proceeded at 25 °C to give a mixture of *trans*-Pt(SR<sup>1</sup>)[C(O)Ph](PPh<sub>3</sub>)<sub>2</sub> (R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>Br-*p*) (*trans*-**10c**) (76%) and *anti*-(PPh<sub>3</sub>)[PhC(O)]Pt(*μ*-SR<sup>1</sup>)<sub>2</sub>Pt[C(O)Ph](PPh<sub>3</sub>) (*anti*-**10c'**) (7%) after 1 h (eq 2).<sup>14</sup> The decarbonylation required more stringent conditions; a solution of isolated *trans*-**10c** (0.01 mmol) in

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(12) The decarbonylation of **1a** (in the absence of **6a**) was not catalyzed at all by Pt(PPh<sub>3</sub>)<sub>4</sub> at 110 °C after 15 h.

(13) Other effective catalysts for the formation of **9a** among those examined were RhCl(PPh<sub>3</sub>)<sub>3</sub> (21%), [RhCl(CO)<sub>2</sub>]<sub>2</sub> (29%), and IrCl(PPh<sub>3</sub>)<sub>2</sub> (CO) (11%).

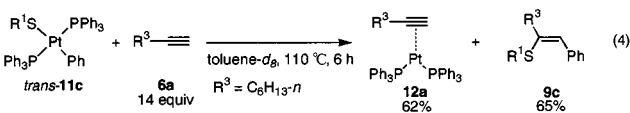
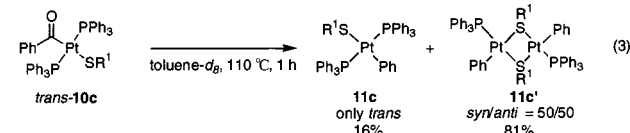
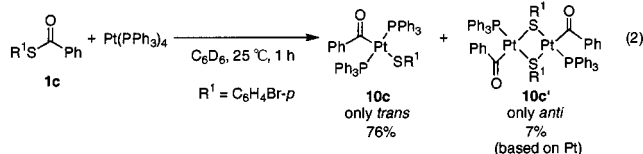
(14) The authentic *trans*-**10c**, *anti*-**10c'**, *trans*-**11c**, and **11c'** were independently prepared and fully characterized by NMR spectra and elementary analyses. The structure of *anti*-**10c'** was unambiguously determined by X-ray analysis. See the Supporting Information for more details.

**Table 1.** The Pt-Catalyzed Carbothiolation of **6** with **1**<sup>a</sup>

run	<b>1</b>	R <sup>1</sup>	R <sup>2</sup>	<b>6</b>	Isolated Yield of <b>9</b> (%)
1	<b>1a</b>	Ph	Ph	<i>n</i> -C <sub>6</sub> H <sub>13</sub> -≡	<b>9a</b> ; 77
2 <sup>b</sup>	<b>1a</b>			<b>6a</b>	<b>9a</b> ; 0 <sup>c</sup>
3	<b>1b</b>	<i>p</i> -tol	Ph	<b>6a</b>	<b>9b</b> ; 70
4	<b>1c</b>	C <sub>6</sub> H <sub>4</sub> Br- <i>p</i>	Ph	<b>6a</b>	<b>9c</b> ; 81
5	<b>1d</b>	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	Ph	<b>6a</b>	<b>9d</b> ; 85
6	<b>1e</b>	Bu	Ph	<b>6a</b>	<b>9e</b> ; 11
7 <sup>d</sup>	<b>1e</b>			<b>6a</b>	<b>9e</b> ; 33
8	<b>1f</b>	CH <sub>2</sub> Ph	Ph	<b>6a</b>	<b>9f</b> ; 13
9 <sup>d</sup>	<b>1f</b>			<b>6a</b>	<b>9f</b> ; 46
10	<b>1g</b>	Ph	<i>p</i> -tol	<b>6a</b>	<b>9g</b> ; 74
11	<b>1h</b>	Ph	C <sub>6</sub> H <sub>4</sub> CN- <i>p</i>	<b>6a</b>	<b>9h</b> ; 79
12	<b>1i</b>	Ph	-CH=CH(Ph)- <i>trans</i>	<b>6a</b>	<b>9i</b> ; 63 <b>9j</b> ; 0
13	<b>1j</b>	Ph	Me	<b>6a</b>	<b>9j</b> ; 0
14	<b>1k</b>	Ph	<i>n</i> -C <sub>6</sub> H <sub>17</sub>	<b>6a</b>	<b>9k</b> ; 0 <sup>e</sup>
15	<b>1c</b>	C <sub>6</sub> H <sub>4</sub> Br- <i>p</i>	Ph	HO(CH <sub>2</sub> ) <sub>4</sub> -≡ <b>6b</b>	<b>9l</b> ; 64
16	<b>1c</b>	C <sub>6</sub> H <sub>4</sub> Br- <i>p</i>	Ph	NC(CH <sub>2</sub> ) <sub>3</sub> -≡ <b>6c</b>	<b>9m</b> ; 78
17	<b>1c</b>	C <sub>6</sub> H <sub>4</sub> Br- <i>p</i>	Ph	Ph-≡ <b>6d</b>	<b>9n</b> ; 71
18 <sup>f</sup>	<b>1c</b>	C <sub>6</sub> H <sub>4</sub> Br- <i>p</i>	Ph	Me <sub>3</sub> Si-≡ <b>6e</b>	<b>9o</b> ; 75
19 <sup>g</sup>	<b>1c</b>	C <sub>6</sub> H <sub>4</sub> Br- <i>p</i>	Ph	≡-(CH <sub>2</sub> ) <sub>4</sub> -≡ <b>6f</b>	<b>9p</b> ; 82

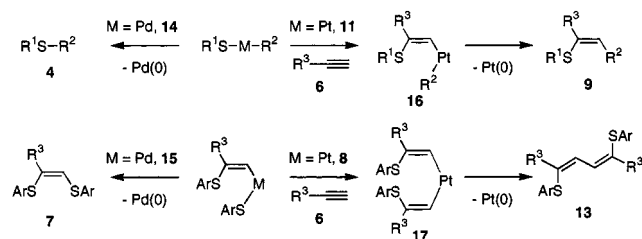
<sup>a</sup> Unless otherwise noted, 1.0 mmol of **1**, 1.2 mmol of **6**, 0.05 mmol of Pt(PPh<sub>3</sub>)<sub>4</sub> under toluene (0.5 mL) reflux for 10–15 h. <sup>b</sup> Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol). <sup>c</sup> PhSPh (**4a**) 40%. <sup>d</sup> Xylenes reflux, 46 h. <sup>e</sup> 2-phenylthio-1-octene (73%). <sup>f</sup> 2.4 mmol of **6e**, 42 h in a sealed tube. <sup>g</sup> 1.2 mmol of **1c**, 0.5 mmol of **6f**.

toluene-*d*<sub>8</sub> (0.6 mL) at 110 °C afforded decarbonylated complexes *trans*-Pt(SAr)(Ph)(PPh<sub>3</sub>)<sub>2</sub> (*trans*-**11c**) (16%) and (Ph)(PPh<sub>3</sub>)Pt(*μ*-SR<sup>1</sup>)<sub>2</sub>Pt(Ph)(PPh<sub>3</sub>) (**11c'**) (*syn/anti* = 50/50) (81% based on Pt) after 1 h (eq 3). The reaction of isolated *trans*-**11c** (0.01 mmol) with **6a** (0.14 mmol) in toluene-*d*<sub>8</sub> (0.5 mL) at 110 °C formed Pt(PPh<sub>3</sub>)<sub>2</sub>(R<sup>3</sup>CCH) (R<sup>3</sup> = C<sub>6</sub>H<sub>13-*n*</sub>) (**12a**) in 62% yield after 6 h (eq 4). It should be noted that *p*-BrC<sub>6</sub>H<sub>4</sub>SPh (**4c**) was not detected at all from the reaction mixture, while **9c** (65%) was obtained, meaning a catalytic cycle of the carbothiolation could be composed of a series of reactions of eqs 2–4.<sup>15–17</sup>

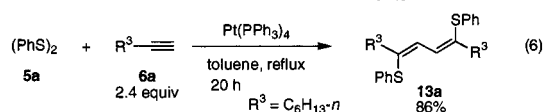
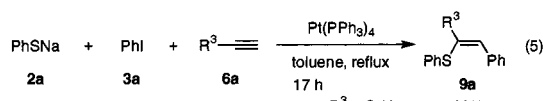


Finally, the generality of the present strategy shown in Scheme 2 was further tested. The reaction of PhSNa (**2a**) (1.1 mmol) with PhI (**3a**) (1.0 mmol)<sup>4b,1</sup> conducted in the presence of **6a** (1.3 mmol)

(15) No intermediate was detected even if the reaction of *trans*-**11c** with **6a** was conducted at 70 °C (70% of **12a** and 72% of **9c** after 62 h).

**Scheme 3.** Proposed Fates of *S*-*M*-*C* units in the Presence of Alkyne

and Pt(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol) under toluene (0.5 mL) reflux for 17 h also generated the desired **9a** in 83% yield (eq 5).<sup>18</sup> Moreover, unlike the case of Pd-catalyzed reaction forming **7**,<sup>5k</sup> the reaction of (PhS)<sub>2</sub> (**5a**) (1.0 mmol) with **6a** (2.4 mmol) performed in the presence of Pt(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol) under toluene (0.5 mL) reflux for 20 h furnished *Z,Z*-R<sup>3</sup>(PhS)C=CHCH=CR<sup>3</sup>(SPh) (R<sup>3</sup> = C<sub>6</sub>H<sub>13-*n*</sub>) (**13a**) in 86% yield (eq 6).



The different outcomes between Pd- and Pt-catalyzed reactions described above can be explained as follows (Scheme 3). Both of the Pd- and Pt-catalyzed reactions would generate similar M(II) complexes with *S*-*M*-*C* fragments such as R<sup>1</sup>S-M-R<sup>2</sup> (M = Pd, **14**; M = Pt, **11**) and M[(*Z*)-CH=C(SAr)(R<sup>3</sup>)](SAr) (M = Pd, **15**; M = Pt, **8**). When M is Pd, after the formation of **14** and **15**, **4** and **7** would be smoothly eliminated without incorporating **6** under toluene reflux condition.<sup>6</sup> In stark contrast, when M is Pt, due to the thermodynamical disadvantage of *S*-sp<sup>2</sup>C bond-forming RE of **4** and **7**, **11** and **8** would have enough lifetime to undergo the regio- and stereoselective IS of **6** into the *S*-Pt bonds to give vinyl platinum **16** and divinyl platinum **17**, leading to the formation of **9** and **13** by the more facile sp<sup>2</sup>C-sp<sup>2</sup>C bond-forming RE from Pt(II).<sup>10,19</sup>

In conclusion, this study provided a simple concept to achieve the transition-metal-catalyzed carbothiolation of alkynes by exploiting contrastive reactivities of thiolate ligands on palladium and platinum complexes. Our continuous efforts will be focused on the extension of the present model to other addition systems.

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**Supporting Information Available:** Experimental procedures, spectral data of the products, and X-ray data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) The reaction of **11c'** (0.005 mmol) with **6a** (0.14 mmol) in the presence of PPh<sub>3</sub> (0.01 mmol) provided 32% of **12a** and 60% of **9c** after 6 h. Because *trans*-**11c** was regenerated by the reaction of **11c'** with PPh<sub>3</sub> in toluene at 110 °C, there may be an equilibrium between **11c** and **11c'**.

(17) Because some unidentified signals together with those of *anti*-**10c'**, *trans*-**11c**, **11c'**, and **12a** were detected in the <sup>31</sup>P NMR spectra of the reaction of *trans*-**10c** with **6a** (14 equiv) at 110 °C, the possibility of the IS of **6** into the complex **10** cannot be precluded at the moment. On the other hand, no reaction took place on a similar treatment of *anti*-**10c'** with **6a** in the absence of PPh<sub>3</sub> at 110 °C.

(18) The reaction with Pd(PPh<sub>3</sub>)<sub>4</sub> instead of Pt(PPh<sub>3</sub>)<sub>4</sub> produced **4a** in 79% yield; however, no formation of **9a** was confirmed.

(19) The failure of carbothiolation in the reactions of runs 13 and 14 in Table 1 may be attributable to sp<sup>2</sup>C-sp<sup>2</sup>C bond-forming RE in the process from **16** to **9**.