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Articles

Platinum-Catalyzed Reaction of Alkynes with ArI (Ar = aryl and thienyl) and Ar′SM (M = Na, K, and Sn(Bu-*n*)$_3$): Three- vs Two-Component Cross-Coupling Reaction

Hitoshi Kuniyasu,* Fumikazu Yamashita, Takayoshi Hirai, Jia-Hai Ye,
Shin-ichi Fujiwara, and Nobuaki Kambe

Department of Molecular Chemistry & Frontier Research Center, Graduate School of Engineering,
Osaka University, Suita, Osaka 565-0871, Japan

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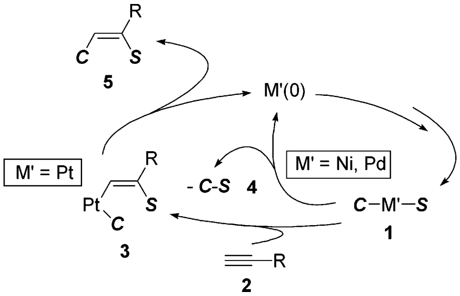
The Pt-catalyzed reactions of terminal alkynes HCCR (**2**) with ArI (**6**) (Ar = aryl and thienyl) and Ar′SM (M = Li, Na, K, and Sn(*n*-Bu$_3$)) (**7**) have been examined. Among them, the combined use of 2- and 3-iodothiophene with PhSK resulted in the formation of (*Z*)-Ar(H)C═C(SAr′)(R) (**5**) in moderate to good yields. When aryl iodide was employed as a coupling partner, thioether ArSAr′ (**4**), a direct cross-coupling product between **6** and **7**, was competitively produced together with **5**. The ratios of formation of **5**/**4** were significantly dependent on the substituent in Ar of **6** and Ar′ of **7** as well as species of **2**. The mechanistic study indicated that **4** was produced by the alkyne-participated reaction of **6** with Pt(Ar)(SAr′)(PPh$_3$)$_2$ (**1**).

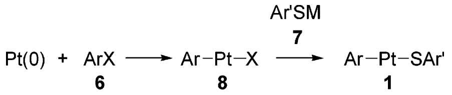
Introduction

Transition metal-catalyzed cross-coupling reactions have served as powerful strategies to build up desired chemical compounds. Along with numerous C−C bond-forming reactions,[1] C−S bond formations have also been developed.[2,3] On the other hand, we have recently reported on a very simple prototype for achievement of a three-component coupling reaction that enabled the regio- and stereoselective introduction of carbon and sulfur functionalities into terminal alkynes. The basic concept is shown in Scheme 1.[4] The generation of platinum complex **1** having a ***C***−Pt−***S*** moiety resistant to C−S bond-forming reductive elimination patterned after the Ni- or Pd-catalyzed syntheses of thioethers **4** sets up the reaction.[2] Then *cis*-insertion of HCCR (**2**) into the Pt−***S*** bond of **1** with Pt bound at the terminal position affords the vinyl platinum complex **3**, possessing a ***C***−Pt−***C*** fragment, and finally ***C***−***C*** bond-forming reductive elimination of vinyl sulfide **5** completes one catalytic cycle to regenerate the Pt(0) complex. According to this working hypothesis, the Pt-catalyzed arylthiolation with aryl thioester,[5a] thienylthiolation with thienyl thioester,[5b] pyridylthiolation with iodopyridine and ArSK,[5c] and furylthiolation with furyl thioester[5d] of **2** have been realized gratifyingly.

Scheme 1. Strategy for Carbothiolation of Alkyne (2)



Scheme 2. Methodology of Generation of 1



$$\mathrm{Pt(0)} + \underset{\mathbf{6}}{\mathrm{ArX}} \longrightarrow \underset{\mathbf{8}}{\mathrm{Ar{-}Pt{-}X}} \xrightarrow{\underset{\mathbf{7}}{\mathrm{Ar'SM}}} \underset{\mathbf{1}}{\mathrm{Ar{-}Pt{-}SAr'}}$$

Herein we wish to report on details about carbothiolation using ArX (Ar = aryl and thienyl; X = Cl, Br, I, and OTf) (**6**) and Ar′SM (M = Li, Na, K, and Sn(Bu-*n*)$_3$) (**7**) as the sources of formation of platinum intermediate **1** (M′ = Pt) via oxidative addition of **6** to Pt(0) to yield the Pt(II) complex Ar−Pt−X (**8**) and subsequent transmetalation with **7** (Scheme 2).[6]

Results and Discussion

Arylthiolation or Thienylthiolation vs Cross-Coupling Reaction (Table 1). First, the arylthiolation of 1-octyne (**2a**,

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* To whom correspondence should be addressed. E-mail: kuni@chem.eng.osaka-u.ac.jp.

[1] *Metal-catalyzed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, 1998.

[2] (a) Kosugi, M.; Shimizu, T.; Migita, T. *Chem. Lett.* **1978**, 13. (b) Murahashi, S.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408. (c) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.; Kato, Y.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1385. (d) Kosugi, M.; Ogata, T.; Terada, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3657. (e) Carpita, A.; Rossi, R.; Scamuzzi, B. *Tetrahedron Lett.* **1989**, *30*, 2699. (f) Cristau, H. J.; Chabaud, B.; Chene, A.; Christol, H. *Synthesis* **1981**, 892. (g) Takagi, K. *Chem. Lett.* **1987**, 2221. (h) Deardorff, D. R.; Linde, R. G.; Martin, A. M.; Shulman, M. J. *J. Org. Chem.* **1989**, *54*, 2759. (i) Martinez, A. G.; Barcina, J. O.; de Fresno, C. A.; Subramanian, L. R. *Synlett*. **1994**, 561. (j) Rane, A. M.; Miranda, E. I.; Soderquist, J. A. *Tetrahedron Lett.* **1994**, *35*, 3225. (k) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551. (l) Cristau, H. J.; Chabaud, B.; Labaudiniere, R.; Christol, H. *Organometallics* **1985**, *4*, 657. (m) Dickens, M. J.; Gilday, J. P.; Mowlem, T. J.; Widdowson, D. A. *Tetrahedron* **1991**, *47*, 8621.

[3] Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205.

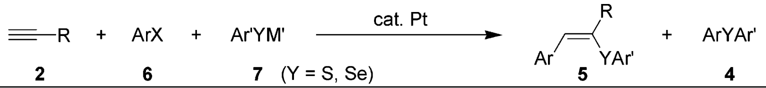
[4] Kuniyasu, H.; Kurosawa, H. *Chem. Eur. J.* **2002**, *8*, 2660.

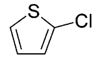
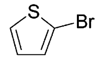
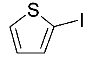
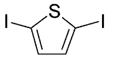
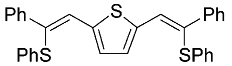
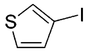
[5] (a) Sugoh, K.; Kuniyasu, H.; Sugae, T.; Ohtaka, A.; Takai, Y.; Tanaka, A.; Machino, C.; Kambe, N.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 5108. (b) Hirai, T.; Kuniyasu, H.; Kambe, N. *Chem. Lett.* **2004**, *33*, 1148. (c) Hirai, T.; Kuniyasu, H.; Kambe, N. *Tetrahedron. Lett.* **2005**, *46*, 117. (d) Hirai, T.; Kuniyasu, H.; Terao, J.; Kambe, N. *Synlett* **2005**, *7*, 1161.

[6] An example of arylthiolation of 1-octyne using PhI and PhSNa has already been reported in a communication (ref 5a).

10.1021/om050340z CCC: $33.50

Table 1. Carbothiolations of 2 with ArX (6) and Ar′YM′ (7)



entry	2	6	7	5^b	4^b
1	$\equiv$—C_6H_{13}-*n* (**2a**)	PhCl (**6a**)	PhSNa (**7a**)	0% (**5a**)	0% (**4a**)
2	**2a**	PhBr (**6b**)	**7a**	0% (**5a**)	0% (**4a**)
3	**2a**	PhI (**6c**)	**7a**	83% (**5a**)	3% (**4a**)
4	**2a**	PhOTf (**6d**)	**7a**	40% (**5a**)	0% (**4a**)
5	**2a**	**6c**	PhSK (**7b**)	87% (**5a**)	5% (**4a**)
6^c	**2a**	**6c**	PhSLi (**7c**)	3% (**5a**)	9% (**4a**)
7	**2a**	**6c**	PhSSn(Bu-*n*)$_3$ (**7d**)	66% (**5a**)	25% (**4a**)
8	**2a**	*p*-MeC_6H_4I (**6e**)	**7a**	63% (**5b**)	4% (**4b**)
9	**2a**	*p*-$CF_3C_6H_4I$ (**6f**)	**7a**	69% (**5c**)	15% (**4c**)
10	**2a**	**6c**	*p*-MeC_6H_4SNa (**7e**)	52% (**5d**)	25% (**4b**)
11	**2a**	**6c**	*p*-$MeOC_6H_4SNa$ (**7f**)	36% (**5e**)	42% (**4d**)
12	**2a**	**6c**	*p*-$CF_3C_6H_4SNa$ (**7g**)	72% (**5f**)	0% (**4c**)
13	**2a**	**6e**	*p*-$MeOC_6H_4SNa$ (**7f**)	53% (**5g**)	35% (**4e**)
14	$\equiv$—$(CH_2)_2CH(CH_3)_2$ (**2b**)	**6c**	**7b**	69% (**5h**)	27% (**4a**)
15	$\equiv$—$(CH_2)_3CN$ (**2c**)	**6c**	**7b**	58% (**5i**)	25% (**4a**)
16	$\equiv$—$(CH_2)_4OH$ (**2d**)	**6c**	**7b**	60% (**5j**)	24% (**4a**)
17	$\equiv$—Ph (**2e**)	**6c**	**7b**	30% (**5k**)	66% (**4a**)
18^d	$\equiv$—$SiMe_3$ (**2f**)	**6c**	**7b**	12% (**5l**)	64% (**4a**)
19	$\equiv$—Si(*i*-Pr)$_3$ (**2g**)	**6c**	**7b**	0% (**5m**)	<1% (**4a**)
20	**2a**	 **6g**	**7b**	0% (**5n**)	0% (**4f**)
21	**2a**	 **6h**	**7b**	72% (**5n**)	0% (**4f**)
22	**2a**	 **6i**	**7a**	51% (**5n**)	0% (**4f**)
23	**2a**	**6i**	**7b**	98% (**5n**)	0% (**4f**)
24^e	**2a**	**6i**	**7c**	3% (**5n**)	0% (**4f**)
25^f	**2a**	**6i**	**7b**	59% (**5n**) (*E*/*Z* = 16/84)	6% (**4f**)
26^f,g	-	**6i**	**7b**	-	93% (**4f**)
27^h	**2e**	 **6j**	**7b**	 54% (**5o**)	
28	**2a**	 **6k**	**7b**	80% (**5p**)	0% (**4g**)
29	**2c**	**6i**	**7b**	75% (**5q**)	< 1% (**4f**)
30	**2d**	**6i**	**7b**	55% (**5r**)	0% (**4f**)
31	**2e**	**6i**	**7b**	86% (**5s**)	7 % (**4f**)
32	$\equiv$—C_6H_4OMe-*p* (**2h**)	**6i**	**7b**	82% (**5t**)	0% (**4f**)
33	$\equiv$—$(CH_2)_2OTHP$ (**2i**)	**6i**	**7b**	57% (**5u**)	0% (**4f**)

[a] **2** (1.2 mmol), **6** (1.0 mmol), **7** (1.1 mmol), Pt$(PPh_3)_4$ (0.05 mmol), and toluene (0.5−1.0 mL) under reflux for 24 h. [b] Isolated yield. [c] $CH_2{=}C(SPh)(C_6H_{13}$-*n*) was produced in 62% yield. [d] 2.5 mmol of **2d** in a sealed tube at 110 °C. [e] $CH_2{=}C(SPh)(C_6H_{13}$-*n*) was produced in 59% yield. [f] Pd$(PPh_3)_4$. [g] Without **2a**. [h] **7b** (2.2 mmol) and **2e** (2.4 mmol).

1.2 mmol) was examined using PhX (**6**, 1.0 mmol) and PhSM (**7**, 1.1 mmol) in the presence of Pt$(PPh_3)_4$ (0.05 mmol) under vigorous toluene reflux for 24 h. Both reactions using PhSNa (**7a**) with PhCl (**6a**) and with PhBr (**6b**) did not produce arylthiolation products (entries 1 and 2), while the reactions using PhI (**6c**) and PhOTf (**6d**) gave the anticipated (*Z*)-Ph(H)C═C(SPh)(C_6H_{13}-*n*) (**5a**) in 83% and 40% yields, respectively (entries 3 and 4).[2a,c]

The reaction of **6c** with PhSK (**7b**) also provided **5a** in 87% yields (entry 5); however, the reaction using PhSLi (**7c**) produced only 3% of **5a** and the hydrothiolation product $CH_2{=}C(SPh)(C_6H_{13}$-*n*)[7] was instead obtained in 62% yield (entry 6). The reaction of **6c** with PhSSn(Bu-*n*)$_3$ (**7d**) yielded **5a** in 66% yield (entry 7).[2d] Interestingly, contrary to the cases of arylthiolation using thioesters,[5a] PhSPh (**4a**), a direct cross-coupling product between **6c** and **7**, can also be furnished under these reaction systems.[8] For example, **4a** was obtained in 3% and 25% yields when **6c** and **7a** or **6c** and **7d** were employed as coupling components (entries 3 and 7). The amount of **4** was significantly influenced by the electronic nature of Ar in **6** and Ar′ in **7**. The introduction of an electron-withdrawing group in Ar of ArI slightly increased the yield of **4** (entry 9; Ar = *p*-$CF_3C_6H_4$, **6f**, 15% of *p*-$CF_3C_6H_4SPh$ (**4c**)) compared to the case of Ph (entry 3; **6c**, 3% of **4a**) or Ar with an electron-donating group (entry 8; Ar = *p*-MeC_6H_4, **6e**, 4% of *p*-MeC_6H_4-SPh (**4b**)). On the other hand, the introduction of electron-donating groups in Ar′ of Ar′SNa increased the formation of **4** (entry 10; Ar′ = *p*-MeC_6H_4, **7e**, 25% of **4b**, entry 11; Ar′ = *p*-$MeOC_6H_4$, **7f**, 42% of **4d**, and entry 13; Ar′ = *p*-$MeOC_6H_4$, **7f**, 35% of **4e**), while an electron-withdrawing group suppressed the generation of **4** (entry 12; Ar′ = *p*-$CF_3C_6H_4$, **7g**, 0% of **4c**). The ratios of **5** and **4** also varied with the species of alkyne (**2**).

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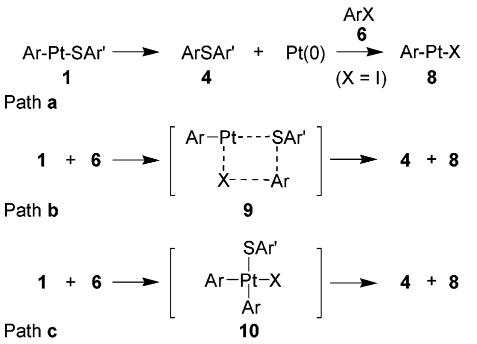
(7) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114,* 5902.

(8) Thioesters were also produced as byproducts under the Pt-catalyzed pyridylthiolation of alkynes by iodopyridine and ArSK. See ref 5c.

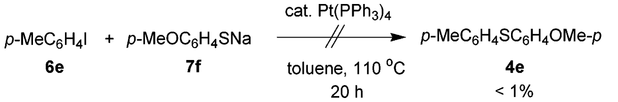
Scheme 3. Possible Reaction Routes to the Formation of 4



The replacement of **2a** for branched aliphatic terminal alkyne **2b** increased the generation of **4** to furnish 69% of **5h** and 27% of **4a** (entry 14 vs entry 5). The arylthiolation of alkynes having −CN and −OH groups also provided the three-component coupling products **5i** and **5j** in moderate yields (entries 15 and 16). When phenyl acetylene (**2e**) and (trimethylsilyl)acetylene (**2f**) were employed, major products were ended in **4a** to yield 30% of **5k** with 66% of **4a** and 12% of **5l** with 64% of **4a**, respectively (entries 17 and 18). Moreover, the formation of **5** and **4** was both totally suppressed when more bulky (triisopropylsilyl)acetylene (**2g**) was employed as the substrate (entry 19), suggesting that the coordination of **2** to the Pt complex must be prerequisite for the formation of thioether (**4**) as well as the production of **5**. Next, the thienylthiolations using ArX and Ar′SM were examined. Although chloride again did not show any activity toward carbothiolation (entry 20), the reaction employing bromide afforded the desired product **5n** in moderate yield (entry 21). On the other hand, the thienylthiolation of **2a** employing 2-iodothiophene (**6g**) with PhSK (**7b**) more efficiently produced desired product **5n** in 98% yield (entry 23). The potassium thiolate exhibited the highest activity among alkali metals examined (entries 22−24). It is a noteworthy fact that palladium complex ($Pd(PPh_3)_4$), which catalyzed the direct cross-coupling reaction between **6g** and **7b** to afford **4f** in good yield (entry 26) and did not catalyze the arylthiolation of alkyne by aryl thioester,[5a] also possessed catalytic activity for thienylthiolation, albeit in lower yield (59%) and with formation of a mixture of stereoisomers ($E/Z = 16/84$) (entry 25).[5b] Thiophene derivative **5o**, with a more extended conjugated moiety, was obtained in 54% yield by employing 2,5-diiodothiophene (entry 27). 3-Thienylthiolation by 3-iodothiophene (**6k**) also successfully proceeded to afford **5p** in 80% yield (entry 28). 2-Thienylthiolation was also successfully applied to other terminal alkynes (**2c**, **2d**, **2e**, $HCCC_6H_4OMe$-*p* (**2h**), and $HCC(CH_2)_2OTHF$ (**2i**)) to give the corresponding three-component coupling products in moderate to good yields (entries 29−33). Again, the formation of **4f**, a direct cross-coupling product between **6i** and **7b**, was fairly suppressed under these thienylthiolations.

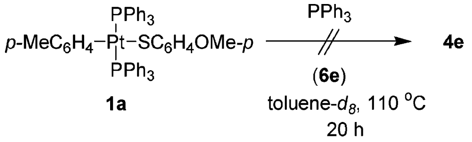
Mechanistic Study: Arylthiolation vs Cross-Coupling Reaction. With respect to the formation of direct cross-coupling product ArSAr′ (**4**), three reaction routes are conceivable (Scheme 3). Path a showed the C−S bond-forming direct reductive elimination of **4** from Pt(II) complex (**1**) with the regeneration of Pt(0), which can be trapped by **6** (X = I) to give **8**. The σ-bond metathesis between the Pt−S bond of **1** and the X−Ar bond of **6** via the four-membered intermediate **9** (path b) and reductive elimination via Pt(IV) intermediate **10** formed by the oxidative addition of **6** to **1** (path c) were also possible. Then to get information about the reaction route to **4**, the following reactions were next examined.

First, the Pt-catalyzed cross-coupling reaction between *p*-MeC_6H_4I (**6e**) and *p*-$MeOC_6H_4SNa$ (**7f**) was attempted; however, only a trace amount of **4e** (<1%) was detected after 20 h at 110 °C (eq 1).

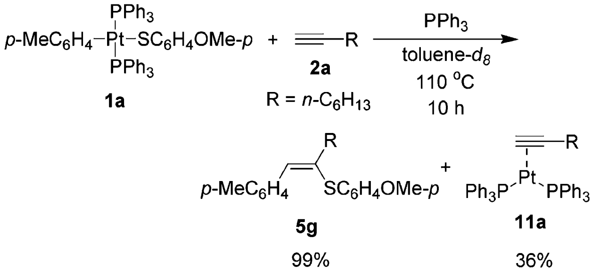


$$p\text{-}MeC_6H_4I + p\text{-}MeOC_6H_4SNa \xrightarrow[\text{toluene, 110 °C, 20 h}]{\text{cat. }Pt(PPh_3)_4} p\text{-}MeC_6H_4SC_6H_4OMe\text{-}p \quad (1)$$

In good accordance with this fact, heating the toluene-d_8 (0.6 mL) solutions of *trans*-$Pt(C_6H_4Me\text{-}p)(SC_6H_4OMe\text{-}p)(PPh_3)_2$ (**1a**, 0.01 mmol)[9] and PPh_3 (0.05 mmol) added as *trans*-to-*cis* isomerization catalyst either in the presence or in the absence of **6e** did not produce *p*-$MeC_6H_4SC_6H_4OMe$-*p* (**4e**) at all (eq 2). It should be noted that 35% of **4e** was produced under the reaction of **2a** with **6e** and **7f** (entry 13 in Table 1).



(2)



(3)

Then the reaction of **1a** with **2a** was monitored by ^1H and ^{31}P NMR spectroscopy (eq 3). After 10 h at 110 °C, the formation of **5g** (99%) and $Pt(PPh_3)_2(HCCR)$ (**11a**; 36%) was confirmed;[10] however, **4e** was again not detected at all. It must also be noted that no signal of suspected vinyl platinum **3** (Scheme 1) was detected during the course of the reaction, presumably because the C−C bond-forming reductive elimination[11] from **3** was much faster than the insertion of **2** into the Pt−S bond of **1**.

With respect to the C−S bond formation from Pd(II) complexes, Hartwig et al. have disclosed that the introduction of an electron-withdrawing group in the detaching carbon functional group and an electron-donating group in the sulfur functional group promoted the reaction.[12] The electronic effects observed in entries 8−13 of Table 1 apparently accord with the electronic nature of C−S bond formation from Pd(II) complexes. However, the above experimental results indicated that the participation of path a of Scheme 3 for the generation of thioether (**4**) was unlikely under the Pt-catalyzed reaction of alkyne (**2**) with ArX (**6**) and Ar′SM (**7**).[13]

Then to examine the possibility of the participation of both **6** and **2** in the formation of **4**, the reaction of *trans*-Pt(C_6H_4-

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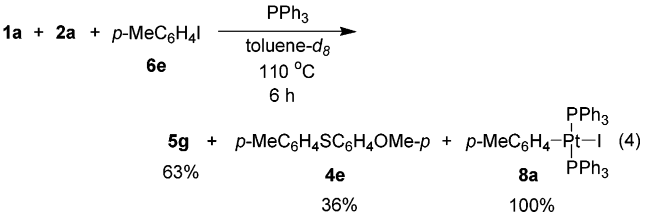
[9] The authentic *trans*-**1**, which was thermodynamically more stable than *cis*-**1**, was successfully prepared by the reaction of $Pt(PPh_3)_4$ with ArI then Ar′SNa.

[10] The low yield of **11a** may be attributable to the formation of $Pt(PPh_3)_4$, which cannot be detected by ^{31}P NMR spectroscopy due to rapid liberation of PPh_3 in solution.

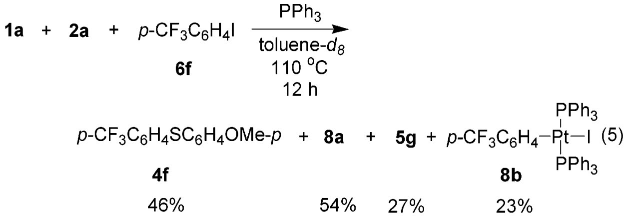
[11] (a) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356. (b) Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972, and references therein.

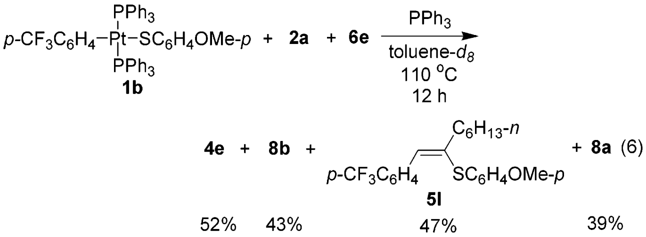
[12] (a) Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205. (b) Baranano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937.

Me-*p*)(SC_6H_4OMe-*p*)($(PPh_3)_2$ (**1a**, 0.01 mmol) with $HCCC_6H_{13}$-*n* (**2a**) (0.1 mmol) was next performed in the presence of *p*-MeC_6H_4I (**6e**, 0.1 mmol) (eq 4). Contrary to the cases of reactions of **1a** with **6e** (eq 2) and **1a** with **2a** (eq 3), the formation of **4e** (36%) was confirmed after 6 h together with **5g** (63% based on SC_6H_4OMe-*p* of **1a**) and *trans*-Pt(C_6H_4Me-*p*)(I)($(PPh_3)_2$ (**8a**, 100% based on Pt).



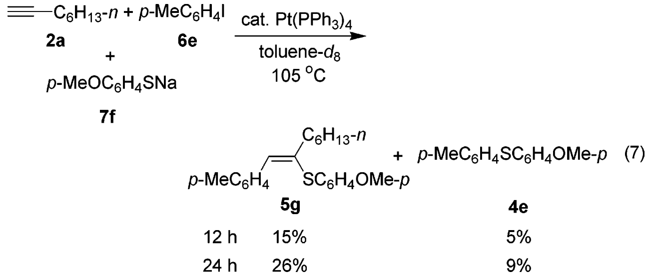
Furthermore, to get insight about the origin of the Ar moiety of Ar−SAr′ (**4**), the reaction of **1a** (0.01 mmol) and **2a** (0.03 mmol) with *p*-$CF_3C_6H_4I$ (**6f**, 0.1 mmol) (eq 5) and the reaction of *trans*-Pt($C_6H_4CF_3$-*p*)(SC_6H_4OMe-*p*)($(PPh_3)_2$ (**1b**, 0.01 mmol) and **2a** (0.03 mmol) with *p*-MeC_6H_4I (**6e**, 0.1 mmol) (eq 6) were next examined.





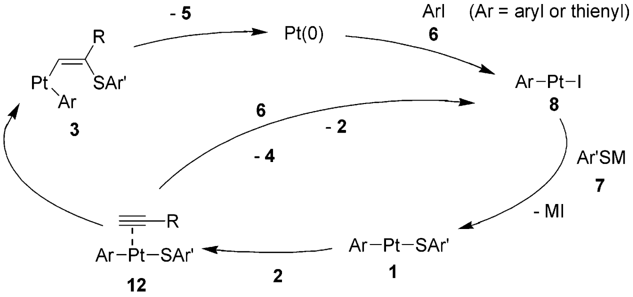
The former produced *p*-$CF_3C_6H_4SC_6H_4OMe$-*p* (**4f**, 46% based on SC_6H_4OMe-*p* of **1a**) and *trans*-Pt(C_6H_4Me-*p*)(I)($(PPh_3)_2$ (**8a**, 54% based on Pt) as well as **5g** (27% based on SC_6H_4OMe-*p* of **1a**) and *trans*-Pt($C_6H_4CF_3$-*p*)(I)($(PPh_3)_2$ (**8b**, 23% based on Pt). On the other hand, the latter produced *p*-$MeC_6H_4SC_6H_4$-OMe-*p* (**4e**, 52% based on SC_6H_4OMe-*p* of **1a**) and **8b** (43% based on Pt) as well as **5l** (47% based on SC_6H_4OMe-*p* of **1a**) and **8a** (39% based on Pt). These results clearly showed that the Ar moiety of **4** was selectively derived from newly added **6**. The facts that the yields of **4f** and **8a** as well as **5g** and **8b** in eq 5 and yields of **4e** and **8b** as well as **5l** and **8a** in eq 6 were all comparable with each other did not contradict the assumption that the formation of these compounds also correlated with each other.

Foregoing data may suggest the involvement of path b of Scheme 3 for the formation of **4**, because the increase of electrophilicity of **6** by introducing an electron-withdrawing group (entry 9 in Table 1) and the increase of nucleophilicity of the SAr′ moiety in **1** by introducing electron-donating substituents (entries 10, 11, and 13 in Table 1) both can accelerate such a polar σ-bond metathesis. However, considering the fact that C−S bond formation of MeSMe took place from the Pt(IV) complex generated by the oxidative addition of MeI to [Pt(SMe)(PMe_2Ph)(μ-SMe)]$_2$,[14] the route of path c cannot be fully ruled out, because the trans ***C***−Pt−***S*** geometry can be retained during the oxidative addition and following reductive elimination sequence.



Finally, the reaction of **2a** (0.12 mmol) with **6e** (0.1 mmol) and **7f** (0.1 mmol) in the presence of $Pt(PPh_3)_4$ (0.01 mmol) in toluene-d_8 (0.6 mL) was monitored by NMR spectroscopy at 105 °C (eq 7). The ^{31}P NMR spectrum taken after 12 h showed the formation of a mixture of **1a** and **8a** in 78% and 5% yields based on Pt, respectively. On the other hand, its ^1H NMR spectrum detected the signals of 15% of **5g** and 5% of **4e**. Then the yields of **5g** and **4e** were increased gradually (26% and 9% after 24 h, respectively), while the yields of **1a** and **8a** hardly changed, indicating that the complexes **1** and **8** existed as resting states of the present Pt-catalyzed reaction. Judging from the foregoing experimental data, possible routes of the present Pt-catalyzed reaction of **2** with **6** and **7** are shown in Scheme 4.

Scheme 4. Possible Reaction Routes to 4 and 5 under the Pt-Catalyzed Reactions of 2 with 6 and 7



After the generation of **1** through the oxidative addition of **6** to Pt(0) and transmetalation with **7**,[15] alkyne **2** would coordinate to **1** to produce **12**, whose formation can be the rate-limiting step of this Pt-catalyzed reaction. The coordinated alkyne may insert into the S−Pt bond to produce **3**, from which C−C bond-forming reductive elimination facilely took place to give **5** with regeneration of Pt(0). When Ar is the aryl group, the complex **12** also competitively could react with **6** to give **8** and **4**, in the latter of which the Ar moiety was selectively incorporated from **6**. This could explain why the product distribution (**5**/**4**) was significantly influenced by the species of alkyne (**2**) and why the yields of **4f** and **8a**, **5g** and **8b**, **4e** and **8b**, and **5l** and **8a** in eqs 5 and 6 were comparable.

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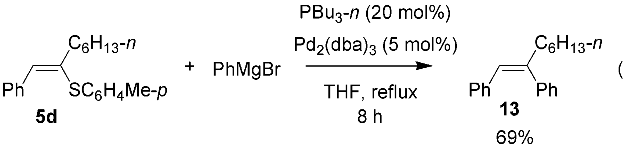
(13) The study of oxidative addition of vinyl sulfide to $Pt(PPh_3)(C_2H_4)$ to yield vinyl platinum with a *cis*-sp^2-C−Pt−S fragment supported that the sp^2-C−S bond-forming reductive elimination was also a thermodynamically unfavorable process even from a *cis*-PPh_3-ligated isomer. Kuniyasu, H.; Ohtaka, A.; Nakazono, T.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2000**, *122*, 2375. See also ref 4.

(14) Puddephatt, R. J.; Upton, C. E. E. *J. Organomet. Chem.* **1975**, *91*, C17.

(15) The reaction of *trans*-Pt(Ph)(I)($(PPh_3)_2$ (**8c**, 0.01 mmol) with **7a** (0.1 mmol) in the presence of PPh_3 (0.1 mmol) in toluene (0.6 mL) produced *trans*-Pt(Ph)(SPh)($(PPh_3)_2$ (**1c**) and [Pt(Ph)(SPh)(PPh_3)]$_2$ (**1c′**) in 34% and 66% yields at 105 °C after 3 h, respectively.

Transformation of 5 into a Double Arylation Product. The utility of the present transformation was attested by converting the SAr group into an Ar group.[2,3,16] The treatment of **5d** (0.5 mmol) with PhMgBr (1.0 mmol) in the presence of $Pd_2(dab)_3 \cdot CHCl_3$ (5 mol %) and PBu_3-*n* (20 mol %) under THF reflux for 8 h resulted in the formation of the desired (*Z*)-(Ph)(H)C═C(Ph)(C_6H_{13}-*n*) (**13**) in 69% yield (eq 8), enabling the introduction of two Ar groups into alkyne **2** by the sequential Pt-catalyzed carbothiolation and Pd-catalyzed cross-coupling reaction.



(8)

Conclusion

This study demonstrated that Pt-catalyzed carbothiolation of terminal alkyne with ArX and Ar′SM can be successfully realized by using 2- and 3-iodothiophene and Ar′SK. When aryl-I was employed as a coupling partner, the carbothiolation can significantly compete with C−S bond formation, where the participation of both alkyne and ArI was indicated. It must be emphasized that catalytic C−S bond-forming cross-coupling may take place through other than conventional direct C−S bond-forming reductive elimination from the M′(II) complex, suggesting that an alternative pathway must always be taken into account, when the mechanisms of a number of transition metal-catalyzed cross-coupling reactions of R−X with R′M are considered.[1]

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra in $CDCl_3$ solution and ^{31}P NMR spectra in toluene-d_8 and benzene-d_6 solution were recorded with a JEOL JNM-Alice-400 (400 MHz). Chemical shifts in the ^1H NMR and ^{13}C NMR spectra were recorded relative to Me_4Si and $CDCl_3$, respectively. Chemical shifts in the ^{31}P NMR spectra were recorded relative to 85% H_3PO_4(aq) as an external standard. Infrared spectra were obtained with a Perkin-Elmer FT-IR (Model 1600). GC mass (EI) analyses were run using a Saturn GCMS-2000 spectrometer. Elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Preparative TLC was carried out using Wakogel B-5F silica gel using hexane and Et_2O as eluent. Toluene was distilled just before use. Aryl iodides, iodothiophene, PhSSn(Bu-*n*)$_3$, and alkynes were commercially available.

General Procedure of Pt-Catalyzed Arylthiolation of Alkynes 2 (entry 3 in Table 1). Into a 3 mL flask equipped with a reflux condenser were added $Pt(PPh_3)_4$ (62.2 mg, 0.05 mmol), PhSNa, (**7a**) (145.4 mg, 1.1 mmol), toluene (0.5 mL), PhI (**6c**) (204.0 mg, 1.0 mmol), and 1-octyne (**2a**) (132.2 mg, 1.2 mmol). The reaction mixture was vigorously refluxed for 24 h under a nitrogen atmosphere, the resulting mixture was filtrated through Celite, and the resultant filtrate was evaporated. The products (**5a**) were isolated by PTLC (eluent: hexane and ether) (83% yield). Other reactions in Table 1 were performed similarly. In the cases of entries 8−13, 1.0 mL of toluene was used as the solvent.

Attempted Reductive Elimination of 4e from 1a (eq 2). Into a dry Pyrex NMR tube were added **1a** (9.5 mg, 0.01 mmol), PPh_3 (13.1 mg, 0.05 mmol), and toluene-d_8 (0.6 mL) under N_2 atmosphere. Then the reaction at 110 °C was monitored by NMR spectroscopy. However, no formation of **4e** was observed even after 20 h. Other mechanistic studies shown in eqs 3−7 were performed similarly.

Supporting Information Available: Experimental procedures and spectral data of the products and authentic **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050340Z

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(16) Itami, K.; Mineno, M.; Muraoka, N.; Yoshida, J. *J. Am. Chem. Soc.* **2004**, *126*, 11778.