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Platinum-Catalyzed Regio- and Stereoselective Arylthiolation of Internal Alkynes

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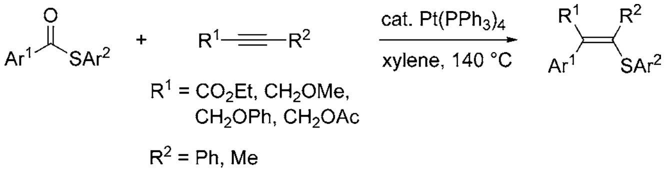
ABSTRACT



Unsymmetrical internal alkynes such as ethyl phenylpropiolate (2b) successfully underwent Pt-catalyzed decarbonylative arylthiolation by thioesters. The regio- and stereoselective insertion of 2b into an S–Pt bond was confirmed by reaction with a platinum complex with an S–Pt–Cl framework.

A number of cis addition reactions of S−X bonds to alkynes with the aid of PR$_3$-ligated group 10 metal complexes have been developed.[1] For S−X bond, S−H,[2] S−S,[3] S−B,[4] S−Si,[5] S−P(O),[6] S−CO$_2$R,[7] S−C(O)Ar,[8] S−CN,[9] and S−C(O)-NR$_2$[10] have been employed as substrates. In most cases, while terminal alkynes underwent regio- and stereoselective additions, internal alkynes were reported to be inert.[11] This paper describes the Pt-catalyzed decarbonylative arylthiolation of internal alkynes by thioesters.[8]

First, the reaction of PhC(O)SPh (**1a**, 0.5 mmol) with 4-octyne (**2a**, 0.6 mmol) was attempted in xylene (0.8 mL) at 140 °C in the presence of Pt(PPh$_3$)$_4$ (0.04 mmol) (entry 1). However, no reaction was confirmed even after 48 h. In stark contrast, the reaction with ethyl phenylpropiolate (**2b**)

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[1] For reviews, see: (a) Kuniyasu, H. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; Wiley-VCH: Zürich, Switzerland, 2001; p 217. (b) Kondo, T.; Mitudo, T. *Chem. Rev.* **2000**, *100*, 3205. (c) Ogawa, A. *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; p 813. (d) Han, L.-B.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1999**, 395. (e) Ogawa, A. *J. Organomet. Chem.* **2000**, *611*, 463. (f) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435. (g) Beletskaya, I. P. *Pure Appl. Chem.* **2005**, *77*, 2021. (h) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (i) Kuniyasu, H.; Kambe, N. *Chem. Lett.* **2006**, *35*, 1320.

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[4] Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219.

[5] Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 8249.

[6] Han, L.-B.; Tanaka, M. *Chem. Lett.* **1999**, 863.

[7] Hua, R.; Takeda, H.; Onozawa, S.; Abe, Y.; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 2899.

[8] (a) Kuniyasu, H.; Kurosawa, H. *Chem. Eur. J.* **2002**, 2660. (b) 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. (c) Hirai, T.; Kuniyasu, H.; Kambe, N. *Tetrahedron. Lett.* **2005**, *46*, 117. (d) Hirai, T.; Kuniyasu, H.; Kambe, N. *Chem. Lett.* **2004**, *33*, 1148. (e) Hirai, T.; Kuniyasu, H.; Terao, J.; Kambe, N. *Synlett* **2005**, 1161. (f) Kuniyasu, H.; Yamashita, F.; Hirai, T.; Ye, J.-H.; Fujiwara, S.; Kambe, N. *Organometallics* **2006**, *25*, 566.

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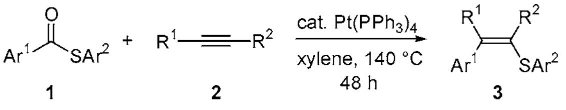
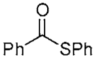
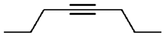
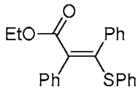
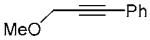
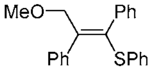
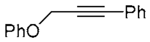
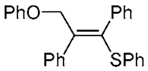
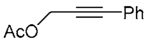
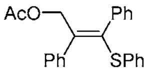
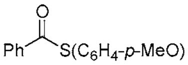
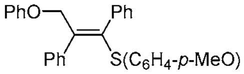
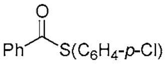
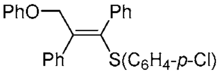
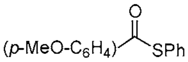
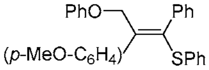
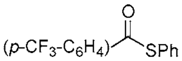
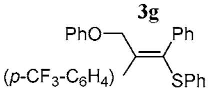
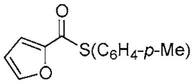
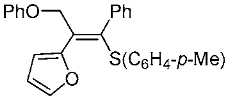
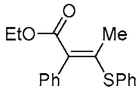
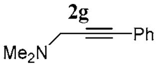
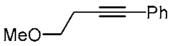
[11] Under phosphine-free Pd-catalyzed hydrothiolation, internal alkynes were also active. See refs 2a and 2c. Recently, Ni-catalyzed thioallylation of terminal and internal alkynes with allyl phenyl sulfide have been reported. See: Hua, R.; Takeda, H.; Onozawa, S-y.; Abe, Y.; Tanaka, M. *Org. Lett.* **2007**, *9*, 263.

10.1021/ol7025069 CCC: $40.75

Table 1. Pt-Catalyzed Arylthiolation of Various Internal Alkynes[a]



entry	thioester **1**	alkyne **2**	product **3**	yield (%)[b]
1	 **1a**	 **2a**	-	n.r.
2	**1a**	$\mathrm{EtOOC{-}{\equiv}{-}Ph}$ **2b**	 **3a**	85%
3	**1a**	 **2c**	 **3b**	78%
4	**1a**	 **2d**	 **3c**	86%
5	**1a**	 **2e**	 **3d**	61%[c]
6	 **1b**	**2d**	 **3e**	87%
7	 **1c**	**2d**	 **3f**	88%
8	 **1d**	**2d**	 **3g**	79%
9	 **1e**	**2d**	 **3h**	85%
10	 **1f**	**2d**	 **3i**	84%
11[d]	**1a**	$\mathrm{EtOOC{-}{\equiv}{-}Me}$ **2f**	 **3j**	49%[c]
12	**1a**	$\mathrm{EtOOC{-}{\equiv}{-}{}^{n}C_6H_{13}}$ **2g**	-	n.r.
13	**1a**	 **2h**	-	n.r.
14	**1a**	 **2i**	-	n.r.

[a] Unless otherwise noted, 0.5 mmol of **1a**, 0.6 mmol of **2**, and 0.04 mmol of Pt $(PPh_3)_4$ in toluene (0.8 mL) at 140 °C for 48 h. [b] Isolated yield. [c] Formation of a small amount of isomer (<3%) was confirmed. [d] 1.6 equiv of **2f** was used.

afforded a colorless solid **3a** in 85% yield (entry 2). Neither regioisomer nor stereoisomer was detected. The X-ray crystallographic analysis of **3a** demonstrated that the SPh of **1a** was bound at the α-carbon of Ph of **2b** and Ph of **1a** at the α-carbon of the EtOC(O) group of **2b** (Figure 1),[12] showing that Pt-catalyzed regio- and stereoselective decarbonylative arylthiolation took place successfully.

A similar transformation was also accomplished by using 1-phenyl-3-methoxy-1-propyne (**2c**) to afford the corresponding adduct **3b** as a sole product whose structure was

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(12) Crystal data for **3a**: space group $P\bar{1}$ (no. 2) with $a = 9.7203(4)$ Å, $b = 9.7299(3)$ Å, $c = 11.1909(4)$ Å, $\alpha = 98.111(1)°$, $\beta = 100.675(1)°$, $\gamma = 106.8189(9)°$, $Z = 2$, $\rho = 1.229$ g/cm^3, $R = 0.061$, and $Rw = 0.172$. See the Supporting Informaion for crystal data for **3b** and **3c**.

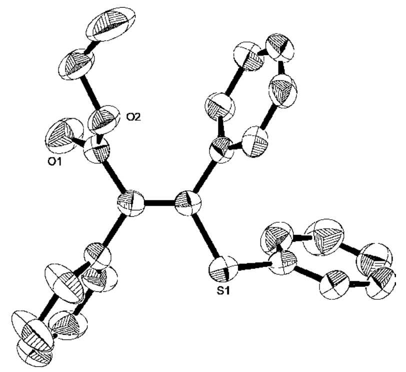


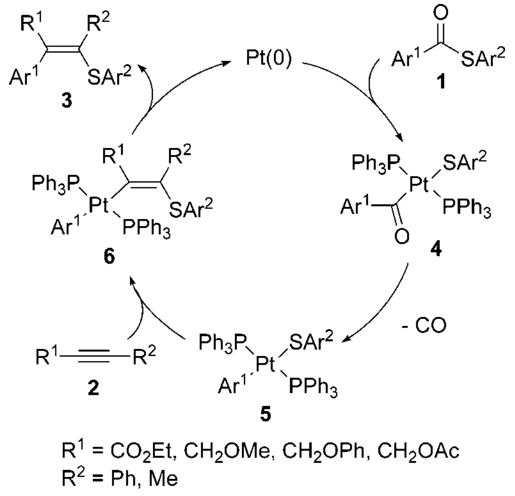
Figure 1. ORTEP diagram of **3a**.

also unambigously determined by X-ray crystallographic analysis (entry 3).[12] Replacement of the MeO group with a PhO or AcO group hardly affected the present Pt-catalyzed decarbonylative arylthiolation (entries 4 and 5). Neither the electron-donating nor the electron-withdrawing group in thioester **1** interfered with the reactions (entries 6−9). The 2-furylthiolation was also acheived to provide the adduct **3i** in 84% yield (entry 10). However, the reaction with aliphatic thioester PhC(O)SCy was totally ineffective.

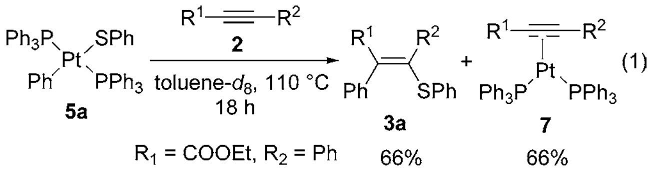
The product of arylthiolation was obtained in 49% yield when EtOC(O)CCMe (**2f**) was used (entry 11). On the other hand, EtOC(O)CC(C_6H_{13}) (**2g**), Me_2NCH_2CCPh (**2h**), and $MeO(CH_2)_2CCPh$ (**2i**) did not show any activity toward the reactions (entries 12−14).

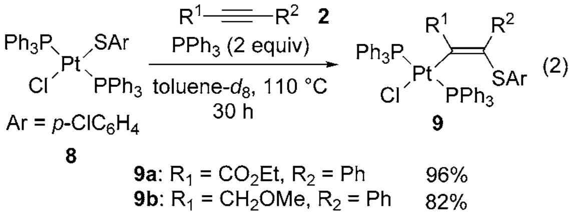
A proposed reaction mechanism for the present Pt-catalyzed decarbonylative arylthiolation of internal alkynes by thioester **1** is shown in Scheme 1. The oxidative addition of **1** to Pt(0) would trigger the reaction to form aroyl platinum **4** and the following decarbonylation would yield aryl platinum **5**.[8b] Then, the regio- and stereoselective insertion of **2** into the platinum−sulfur bond of **5** would generate vinyl platinum **6**. Finally, C−C bond-forming reductive elimination of **3** would occur to regenerate Pt(0) complex.

Scheme 1. Proposed Mechanism for the Pt-Catalyzed Decarbonylative Addition of Thioester to Internal Alkynes



Thus, to obtain information about the reactivity of **2** toward **5**, the stoichiometric reaction of complex $Pt(SPh)(Ph)(PPh_3)_2$ (**5a**) with **2b** was monitored by ^1H and ^{31}P NMR spectroscopy in toluene-d_8 at 110 °C (eq 1). After 18 h, the formation of arylthiolation product **3a** and alkyne-coordinated platinum(0) complex **7** was confirmed in 66% yields, showing that complex **5** is involved as an intermediate in the catalytic cycle.





To confirm the regio- and stereochemistry of the insertion of **2** into the S−Pt bond, the reaction of platinum complex $Pt(SC_6H_4\text{-}p\text{-}Cl)(Cl)(PPh_3)_2$ (**8**) with **2b** was carried out in toluene-d_8 at 110 °C.[13] The ^{31}P NMR spectrum taken after 30 h indicated the formation of vinyl platinum complex **9a** in 96% yield (eq 2) on the basis of a signal at δ 23.3 ppm (s, J_{Pt-P} = 3044 Hz). The reaction of complex **8** with **2c** under the same conditions afforded a similar vinyl platinum **9b** in 82% yield. The structures of **9a** and **9b** were unambiguously determined by X-ray crystallographic analyses, elucidating that the double bonds of vinyl platinums have *Z*-configuration with Pt at the α-carbon of CO_2Et or CH_2OMe groups (Figure 2 and 3).[14] Both the regio- and stereoselectivity were consistent with those anticipated from the structure of **6**. It must be noted that the Pt−O distances

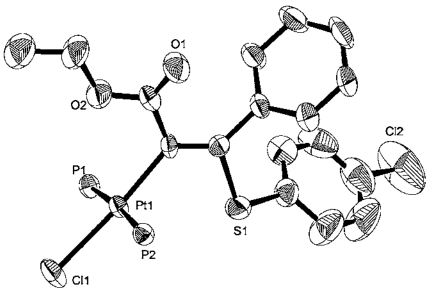


Figure 2. ORTEP diagram of vinyl platinum complex **9a**. Ph groups of PPh_3 and a solvent molecule are omitted for clarity. Selected bond lengths [Å]: Pt−C 2.022(6), Pt−Cl1 2.382(2), Pt−P1 2.307(1), Pt−P2 2.317(1), Pt−O2 3.028(4).

of **9a** (3.0 Å) and **9b** (3.0 Å) are within the sum of the van der Waals radii (3.2 Å) of the two atoms, implying that the interaction between Pt and O atoms plays a crucial role in achieving regioselective insertion of **2** into the S−Pt bonds of **5** or **8**.

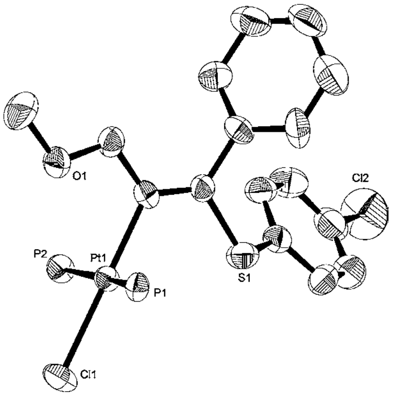


Figure 3. ORTEP diagram of vinyl platinum complex **9b**. Ph groups of PPh_3 are omitted for clarity. Selected bond lengths [Å]: Pt−C 2.05(1), Pt−Cl1 2.398(3), Pt−P1 2.320(3), Pt−P2 2.298(3), Pt−O1 2.960(9).

In summary, this study demonstrated that some internal alkynes exhibited high catalytic activity as substrates of Pt-catalyzed decarbonylative arylthiolation by thioesters. This reaction can be achieved by introduction of the oxygen-containing group in alkynes at the proper position. Catalytic activities of internal alkynes for other transition-metal-catalyzed S−X activations are under investigation.

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Supporting Information Available: Experimental procedures and characterization data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Recently, we have reported that the insertion was directly observed by the reaction of terminal alkynes with $Pt(SAr)(Cl)(PPh_3)_2$. Kuniyasu, H.; Yamashita, F.; Terao, J.; Kambe, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 5929.

(14) Crystal data for **9a**: space group $P2_1/n$ (no. 14) with $a = 12.1258(2)$ Å, $b = 12.6152(3)$ Å, $c = 34.5793(7)$ Å, $\beta = 100.5756(7)°$, $Z = 4$, $\rho = 1.514$ g/cm^3, $R = 0.040$, and $Rw = 0.085$. Crystal data for **9b**: space group $Pna2_1$ (no. 33) with $a = 39.9145(7)$ Å, $b = 11.9216(3)$ Å, $c = 9.4584(2)$ Å, $\beta = 101.6122(9)°$, $Z = 4$, $\rho = 1.542$ g/cm^3, $R = 0.044$, and $Rw = 0.118$.