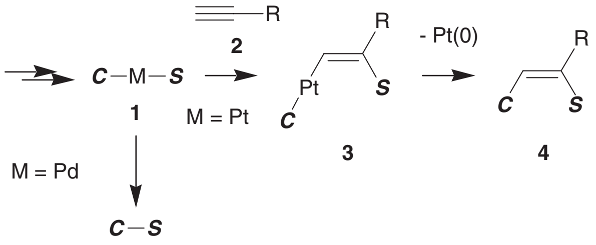
Pt-Catalyzed Regio- and Stereoselective Thienylthiolation of Alkynes

Takayoshi Hirai, Hitoshi Kuniyasu,* and Nobuaki Kambe*
Department of Molecular Chemistry & Frontier Research Center, Graduate School of Engineering,
Osaka University, Suita, Osaka 565-0871

(Received June 23, 2004; CL-040728)

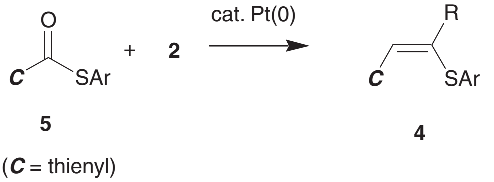
The Pt-catalyzed decarbonylative thienylthiolation of terminal alkynes by thienylthioesters took place regio- and stereoselectively under toluene reflux to give vinylsulfides with *cis*-thienyl group at β-carbon in moderate to good yields.

Transition-metal catalyzed simultaneous introductions of carbon and heteroatom functionalities to C–C unsaturated bonds have provided straightforward strategies to produce highly functionalized organic compounds. The carbosilylation,[1] carbostannylation,[2] and carbochlorination[3] of alkynes are among the most successful examples. On the other hand, we have recently disclosed that the Pt-catalyzed regio- and stereoselective carbothiolation of terminal alkynes has been achieved by exploiting contrastive reactivities of *C* and *S* ligands on Pd and Pt complexes.[4] The basic concept is shown in Scheme 1, comprising: (1) generation of platinum complex **1** having *C*–Pt–*S* moiety produced after the Pd-catalyzed C–S bond-forming reactions,[5] (2) conversion of **1** into the vinyl complex **3** possessing *C*–Pt–*C* fragment by the *cis*-insertion of HCCR (**2**) into the Pt–S bond of **1** with Pt bound at the terminal position,[6] and (3) subsequent *C*–*C* bond-forming reductive elimination from **3** to afford vinyl sulfide **4** with regeneration of Pt(0) complex.[7,8] For example, the Pt-catalyzed arylthiolation and vinylthiolation of **2** were realized using *C*C(O)SAr (*C* = aryl or vinyl) with the Pd-catalyzed decarbonylations as model reactions.[9]



Scheme 1. Strategy for carbothiolation of alkynes.

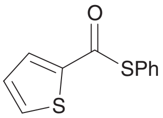
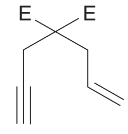
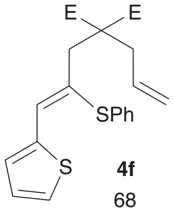
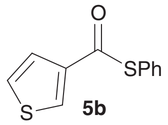
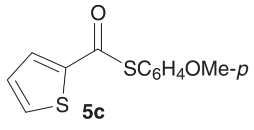
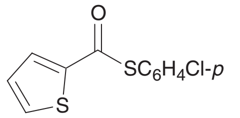
Herein we wish to report on the thienylthiolation, an extended type of Pt-catalyzed carbothiolation using thienylthioesters (**5**) as substrates (Eq 1).



(1)

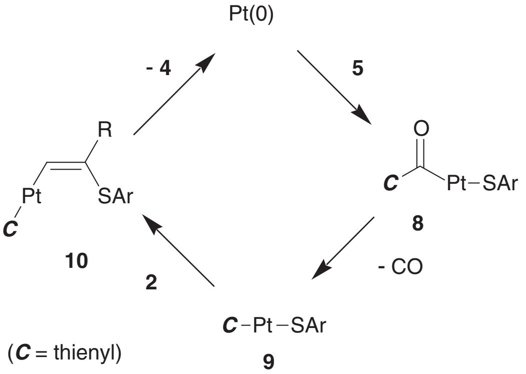
First, the reaction of (2-thienyl)C(O)SPh (**5a**, 1.0 mmol) with 1-octyne (**2a**, 1.2 mmol) in toluene (0.5 mL) was carried out in the presence of Pt(PPh$_3$)$_4$ (0.05 mmol) under reflux for 24 h. The anticipated *Z*-(2-thienyl)CH=C(*n*-C$_6$H$_{13}$)(SPh) (**4a**) was obtained in 88% yield together with 7% of (2-thienyl)(*n*-C$_6$H$_{13}$)C=CHCH=C(SPh)(*n*-C$_6$H$_{13}$) (**6a**) (Entry 1 in

Table 1. Pt-catalyzed thienylthiolation of **2** by **5**[a]

Entry	5	2	Isolated Yield (%) of 4	
1	 **5a**	$\equiv$—C_6H_{13}-*n* **2a**	**4a**	88[b]
2	**5a**	$\equiv$—Ph **2b**	**4b**	80
3	**5a**	$\equiv$—C_6H_4OMe-*p* **2c**	**4c**	78
4	**5a**	$\equiv$—$(CH_2)_3CN$ **2d**	**4d**	85
5	**5a**	$\equiv$—$(CH_2)_4OH$ **2e**	**4e**	85
6	**5a**	 **2f**	 **4f**	68
7[c]	**5a**	$\equiv$—$SiMe_3$ **2g**	**4g**	89
8	**5a**	H_7C_3—$\equiv$—C_3H_7 **2h**	**4h**	nd[d]
9	**5a**	$\equiv$—CH_2Br **2i**	**4i**	nd[d,e]
10	 **5b**	**2a**	**4j**	84
11	 **5c**	**2a**	**4k**	76
12	 **5d**	**2a**	**4l**	46

[a] **5** (1.0 mmol), **2** (1.2 mmol), and Pt(PPh$_3$)$_4$ (0.05 mmol) in toluene (0.5 mL) at 110 °C for 24 h. [b] 7% of (2-thienyl)RC=CHCH=C(SPh)(R) (**6a**). [c] 2.5 mmol of **2g**, 24 h in a sealed tube. [d] Not detected. [e] CH$_2$=C(SPh)(CH$_2$Br) (12%).

Table 1).[10] However, neither isomer of **4a** nor thioether (2-thienyl)SPh (**7a**) was detected.[11] It must be noted that Pd-complex also possessed some catalytic ability in the present thienylthiolation: 38% of **4a** as well as 25% of **7a** and 2% of **6a** was produced when $Pd(PPh_3)_4$ was employed as a catalyst. The scope and limitations of the present Pt-catalyzed thienylthiolation of alkynes were summarized in Table 1. Phenylacetylene and its derivative (**2b** and **2c**) also underwent the thienylthiolation to give the corresponding decarbonylative adducts **4b** and **4c**, which have significantly extended π-conjugation systems in moderate yields (Entries 2 and 3). Some functional groups such as cyano and hydroxy groups were tolerant toward the present transformation (Entries 4 and 5). When an alkyne (**2f**) with a tethered olefin unit was employed, the chemoselective addition took place at the triple bond (Entry 6). The reaction using trimethylsilylacetylene (**2g**) gave the thienylthiolation product in good yield (Entry 7). However, internal alkyne (**2h**) and propargyl bromide (**2i**) were totally ineffective (Entries 8 and 9). The 3-thienylthiolation using (3-thienyl)C(O)SPh (**5b**) also occurred to give the corresponding adduct **4j** in 84% yield (Entry 10). The compounds such as (2-thienyl)C(O)(SC_6H_4OMe-*p*) (**5c**) and (2-thienyl)-C(O)(SC_6H_4Cl-*p*) (**5d**) also can be used as reagents for thienylthiolation of **2** (Entries 11 and 12).



Scheme 2. A Plausible reaction route.

A plausible reaction route is shown in Scheme 2, which includes the oxidative addition of **5** to Pt(0) to form Pt(**C**)[C(O)-SAr] (**C** = thienyl) (**8**), decarbonylation to give the complex **9**, insertion of **2** into the Pt–S bond to furnish **10**, and subsequent reductive elimination of **4** from **10** with regeneration of Pt(0). In fact, when the reaction of **5a** (0.01 mmol) with $Pt(PPh_3)_4$ (0.01 mmol) was carried out in toluene-d_8 (0.5 mL), the oxidative addition of **5a** to $Pt(PPh_3)_4$ proceeded at ambient temperature to give a mixture of *trans*-Pt(SPh)[C(O)(2-thienyl)]$(PPh_3)_2$ (**8a**) (45%) and it's dimeric (PPh_3)[(2-thienyl)C(O)]Pt(μ-SPh)$_2$Pt[C(O)(2-thienyl)](PPh_3) (**8a′**) (55%) after 1.5 h. The decarbonylation required more stringent conditions; leaving the solution of **8a** and **8a′** at 110 °C for 1 h afforded decarbonylated complexes *trans*-Pt(SPh)(2-thienyl)$(PPh_3)_2$ (**9a**) (30%) and (2-thinyl)(PPh_3)Pt(μ-SPh)$_2$Pt(2-thienyl)(PPh_3) (**9a′**) (70% based on Pt). Finally, heating the solution for 6 h after the addition of **2a** (0.012 mmol) at 110 °C resulted in the formation of **4a** in 89% yield.

In conclusion, this paper revealed that the Pt-catalyzed carbothiolation prototype also could be successfully applied to the novel thienylthiolation. Further study to testify the generality of carbothiolation chemistry is now under investigation.

Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining mass spectra with a JEOL JMS-DX303 instrument.

References and Notes

1 a) N. Chatani, N. Amishiro, and S. Murai, *J. Am. Chem. Soc.*, **113**, 7778 (1991). b) N. Chatani, N. Amishiro, T. Mori, T. Yamashita, and S. Murai, *J. Org. Chem.*, **60**, 1834 (1995). c) Y. Obora, Y. Tsuji, and T. Kawamura, *J. Am. Chem. Soc.*, **115**, 10414 (1993). d) Y. Obora, Y. Tsuji, and T. Kawamura, *J. Am. Chem. Soc.*, **117**, 9814 (1995). e) S. Nii, J. Terao, and N. Kambe, *J. Org. Chem.*, **65**, 5291 (2000). f) S. Nii, J. Terao, and N. Kambe, *J. Org. Chem.*, **69**, 573 (2004).

2 H. Yoshida, E. Shirakawa, Y. Nakano, Y. Honda, and T. Hiyama, *Bull. Chem. Soc. Jpn.*, **74**, 637 (2001) and references sited therein.

3 K. Kokubo, K. Matsumasa, M. Miura, and M. Nomura, *J. Org. Chem.*, **61**, 6941 (1996).

4 a) H. Kuniyasu and H. Kurosawa, *Chem.—Eur. J.*, **8**, 2660 (2002). b) K. Sugoh, H. Kuniyasu, T. Sugae, A. Ohtaka, Y. Takai, A. Tanaka, C. Machino, N. Kambe, and H. Kurosawa, *J. Am. Chem. Soc.*, **123**, 5108 (2001). c) T. Hirai, H. Kuniyasu, T. Kato, Y. Kurata, and N. Kambe, *Org. Lett.*, **5**, 3871 (2003).

5 a) G. Mann, D. Barannaro, J. F. Hartwig, A. L. Rheingold, and L. A. Guzei, *J. Am. Chem. Soc.*, **120**, 9205 (1998). b) T. Kondo and T. Mitsudo, *Chem. Rev.*, **100**, 3205 (2000).

6 Although quite a few papers, describing the participation of the insertion of alkynes into S–M (M = Pd and Pt) bonds as elementary reactions have been reported, information about the process has been actually very limited. a) H. Kuniyasu, in “Catalytic Heterofunctionalization,” ed. by A. Togni and H. Grützmacher, Wiley, Zürich, Switzerland (2001), Chap. 7, p 217. b) K. Sugoh, H. Kuniyasu, and H. Kurosawa, *Chem. Lett.*, **2002**, 106.

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

8 For the synthetic utility of vinyl sulfides, see: a) B. M. Trost and A. C. Lavoie, *J. Am. Chem. Soc.*, **105**, 5075 (1983). b) P. Magnus and D. Quagliato, *J. Org. Chem.*, **50**, 1621 (1985).

9 K. Osakada, T. Yamamoto, and A. Yamamoto, *Tetrahedron Lett.*, **28**, 6321 (1987).

10 General procedure: Into a two-necked flask were placed **5a** (1.0 mmol), $Pt(PPh_3)_4$ (0.05 mmol), toluene (0.5 mL), and then **2a** (1.2 mmol). After the reaction mixture was vigorously refluxed for 24 h, the reaction mixture was separated by PTLC using hexane as an eluent to provide **4a** and **6a** in 88% and 7% (based on **5**), respectively. (*Z*)-**4a** (run 1, Table 1): light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.39 (m, 2H), 7.38–7.12 (m, 5H), 6.99 (s, 1H), 6.96–6.89 (m, 1H), 2.29 (t, $J = 7.6$ Hz, 2H), 1.58–1.50 (m, 2H), 1.28–1.17 (m, 6H), 0.85 (t, $J = 6.8$ Hz, 3H); NOE experiment: Irradiation of the aryl triplet at δ 2.29 resulted in a 7.8% enhancement of the signal at δ 6.99 (C-1 vinyl singlet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.77, 134.00, 132.49, 129.95, 129.10, 128.72, 127.37, 126.36, 126.19, 125.79, 38.30, 31.64, 28.86, 28.59, 22.62, 14.19; IR (NaCl) 3071, 2954, 2928, 2855, 1582, 1476, 1439, 1377, 1361, 1315, 1216, 1068, 1050, 1024, 1000, 854, 818, 741, 699 cm^{-1}; mass spectrum (EI) m/z 302 (M^+, 100); Anal. Calcd for $C_{18}H_{22}S_2$: C, 71.47; H, 7.33; S, 21.20. Found: C, 71.38; H, 7.33; S, 20.96. The regiochemistry was determined by C–C 2-D NMR experiment.

11 $Pt(PPh_3)_4$ did not catalyze the decarbonylation of **5a** at all under toluene reflux for 24 h.