

Pt-Catalyzed Regio- and Stereoselective Thienylthiolation of Alkynes

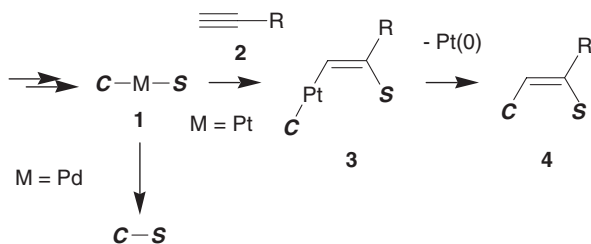
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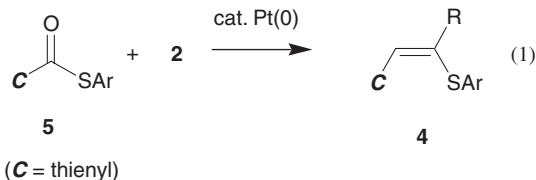
The Pt-catalyzed decarbonylative thienylthiolation of terminal alkynes by thienylthioesters took place regio- and stereoselectively under toluene reflux to give vinylsulfides with *cis*-thienyl group at β -carbon in moderate to good yields.

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 carbochlorination³ 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 CC(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).



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(PPh₃)₄ (0.05 mmol) under reflux for 24 h. The anticipated *Z*-(2-thienyl)CH=C(*n*-C₆H₁₃)(SPh) (**4a**)

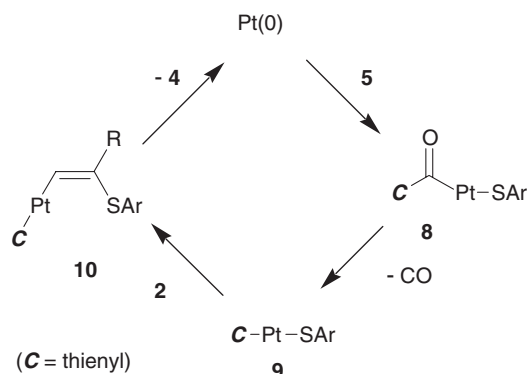
was obtained in 88% yield together with 7% of (2-thienyl)-(*n*-C₆H₁₃)C=CHCH=C(SPh)(*n*-C₆H₁₃) (**6a**) (Entry 1 in

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

Entry	5	2	Isolated Yield (%) of 4
1			4a 88 ^b
2	5a		4b 80
3	5a		4c 78
4	5a		4d 85
5	5a		4e 85
6	5a		 4f 68
7 ^c	5a		4g 89
8	5a		4h nd ^d
9	5a		4i nd ^{d,e}
10		2a	4j 84
11		2a	4k 76
12		2a	4l 46

^a**5** (1.0 mmol), **2** (1.2 mmol), and Pt(PPh₃)₄ (0.05 mmol) in toluene (0.5 mL) at 110 °C for 24 h. ^b7% of (2-thienyl)RC=CHCH=C(SPh)(R) (**6a**). ^c2.5 mmol of **2g**, 24 h in a sealed tube. ^dNot detected. ^eCH₂=C(SPh)(CH₂Br) (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(PPh₃)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)(SC₆H₄OMe-*p*) (**5c**) and (2-thienyl)-C(O)(SC₆H₄Cl-*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(PPh₃)₄ (0.01 mmol) was carried out in toluene-*d*₈ (0.5 mL), the oxidative addition of **5a** to Pt(PPh₃)₄ proceeded at ambient temperature to give a mixture of *trans*-Pt(SPh)[C(O)(2-thienyl)](PPh₃)₂ (**8a**) (45%) and its dimeric (PPh₃)₂[(2-thienyl)C(O)]Pt(μ -SPh)₂Pt[C(O)(2-thienyl)](PPh₃) (**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)(PPh₃)₂ (**9a**) (30%) and (2-thienyl)(PPh₃)Pt(μ -SPh)₂Pt(2-thienyl)(PPh₃) (**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.

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- General procedure: Into a two-necked flask were placed **5a** (1.0 mmol), Pt(PPh₃)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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₁₈H₂₂S₂: 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.
- Pt(PPh₃)₄ did not catalyze the decarbonylation of **5a** at all under toluene reflux for 24 h.