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The Pt-Catalyzed Carboselenation of Alkynes by Selenoesters

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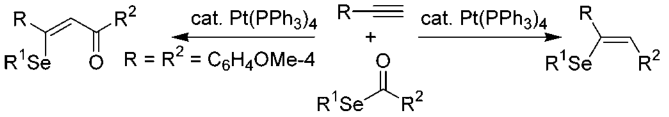
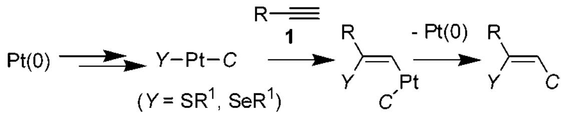
ABSTRACT



The Pt-catalyzed carboselenation of terminal alkynes with selenoesters provided vinylselenides regio- and stereoselectively in moderate yields.

Although the transition-metal-catalyzed additions of heteroatom-containing compounds to C−C unsaturated compounds represented by hydrosilylation have been studied for more than three decades,[1] the utilities of organochalcogenides with *Y*−*X* bonds (*Y* = SR^1, SeR^1; *X* = element or functional group) have been recognized only lately.[2] We have recently demonstrated that basic knowledge of the ligand behavior of thiolates on Pd and Pt complexes[3] could be exploited to develop new reactions, that is, the Pt-catalyzed carbothiolation of alkynes RCCH (**1**).[4] The concept we have elucidated is quite simple: (1) formation of an intermediate with the *S*−Pt−*C* fragment patterned after Pd-catalyzed *S*−*C* bond-forming cross-coupling reaction;[5] (2) insertion of **1** into the *S*−Pt bond to furnish a complex with a vinyl−*C*−Pt−*C* fragment; and (3) vinyl−*C*−*C* bond-forming reductive elimination with regeneration of Pt(0) (Scheme 1, *Y* = SR^1). Herein we wish to report on the Pt-catalyzed carboselenation of **1**, an extension of the protocol to selenium analogues (*Y* = SeR^1).[6]

Scheme 1. Schematic Strategy for Carbothiolation and Carboselenation of **1**



First, the reaction of 1-octyne (**1a**) (1.2 mmol) with PhSeC(O)Ph (**2a**) (1.0 mmol) was carried out in the presence 0.05 mmol of Pt(PPh$_3$)$_4$ in toluene (0.5 mL) under vigorous reflux conditions for 20 h. The crude reaction mixture was then subjected to preparative TLC. The anticipated *Z*-(*n*-C$_6$H$_{13}$)(PhSe)C=CH(Ph) (**3a**),[7] the product of *decarbonylative arylselenation*, was isolated in 89% yield (entry 1 of Table 1). Neither the regio- and stereoisomers of **3a** nor PhSePh

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[1] (a) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Sillicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley-Intercience: Chishester, UK, 1989; Chapter 29. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 523.

[2] Kuniyasu, H. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H. Eds.; Wiley: Zürich, Switzerland, 2001; p 217.

[3] (a) Kuniyasu, H.; Sugoh, K.; Moon, S.; Kurosawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4669. (b) Kuniyasu, H.; Ohtaka, A.; Nakazono, T.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2000**, *122*, 2375.

[4] (a) Kuniyasu, H.; Kurosawa, H. *Chem. Eur. J.* **2002**, *8*, 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.

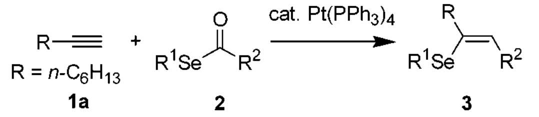
[5] Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205.

[6] The Pd-catalyzed *Se*−*C* bond-forming reductive elimination has been reported. (a) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796. (b) Beletskaya, I. P.; Sigeev, A. S.; Peregudov, A. S.; Petrovskii, P. V. *J. Organomet. Chem.* **2000**, *605*, 96. (c) Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725.

[7] The stereo- and regiochemistry of **3a** were determined by NOE and the value of $J_{\mathrm{C-Se}}$, respectively. Cullen, E. R.; Guziec, F. S.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Chem. Soc., Perkin Trans. 2* **1982**, 473.

10.1021/ol0354223 CCC: $25.00

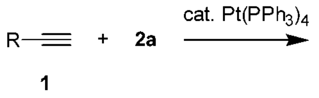
Table 1. The Pt-Catalyzed Carboselenation of **1a** with **2**[a]



entry	2	R^1	R^2	isolated yield of **3** (%)
1	**2a**	Ph	Ph	**3a**; 89
2[b]	**2a**	Ph	Ph	**3a**; 0[c]
3	**2b**	4-$CF_3C_6H_4$	Ph	**3b**; 80
4	**2c**	4-MeC_6H_4	Ph	**3c**; 81
5	**2d**	Ph	$C_6H_4CF_3$-4	**3d**; 68[d]
6	**2e**	Ph	$C_6H_3Cl_2$-2,4	**3e**; 83
7	**2f**	Ph	C_6H_4OMe-4	**3f**; 65[e]
8[f]	**2g**	4-$MeOC_6H_4$	C_6H_4OMe-4	**3g**; 81[g]
9	**2h**	Ph	*trans*-C(H)=C(H)Ph	**3h**; 35
10[h]	**2i**	Ph	C(H)=CMe_2	**3i**; 24
11[h]	**2j**	4-MeC_6H_4	*t*-Bu	**3j**; 0

[a] Unless otherwise noted, 1.2 mmol of **1a**, 1.0 mmol of **2**, and 0.05 mmol of $Pt(PPh_3)_4$ under toluene (0.5 mL) reflux for 20−40 h. [b] $Pd(PPh_3)_4$ (0.05 mmol). [c] PhSePh (**4a**) 72%. [d] 2-(Phenylseleno)-1-octene (18%). [e] *Z*-(*n*-C_6H_{13})(R^1Se)C=C(H)C(O)(R^2) (**5a**) (11%). [f] 40 h. [g] **5b** (9%). [h] 7 days.

Table 2. The Pt-Catalyzed Carboselenation of **1** with **2a**[a]



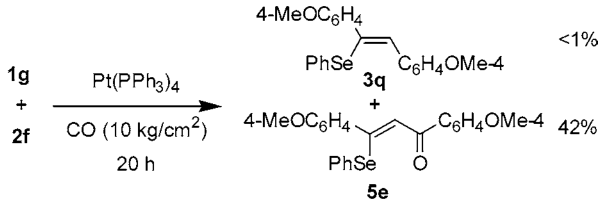
entry	1	R	isolated yield of **3** (%)
1	**1b**	$PhCH_2$	**3k**; 72
2	**1c**	$HO(CH_2)_3$	**3l**; 56[b]
3	**1d**	HO(1-cyclohexyl)	**3m**;86
4	**1e**	$NC(CH_2)_3$	**3n**; 68
5	**1f**	Ph	**3o**; 61[c,d]
6	**1g**	4-$MeOC_6H_4$	**3p**; 31[e,f]

[a] 1.2 mmol of **1**, 1.0 mmol of **2**, and 0.05 mmol of $Pt(PPh_3)_4$ under toluene (0.5 mL) reflux for 20−30 h. [b] *E*/*Z* = 5/95. [c] **3o** *E*/*Z* = 10/90. [d] **5c** (19%). [e] **3p** *E*/*Z* = 12/88. [f] **5d** (31%).

(**4a**) was obtained. In stark contrast, when the reaction was performed with $Pd(PPh_3)_4$ instead of $Pt(PPh_3)_4$, **3a** was hardly obtained (<1%) and the major product was **4a** (72%), indicating that *Se*−*C* bond-forming reductive elimination was facile from the Pd(II) complex after decarbonylation even in the presence of **1a** (entry 2).[6] The results of the reactions of **1a** with various $R^1SeC(O)R^2$ (**2**) are summarized in Table 1. All reactions performed with electron-withdrawing or -donating groups in aromatic rings in R^1 and R^2 provided the desired arylselenation products as major products (entries 3−8). When $PhSeC(O)C_6H_4CF_3$-4 (**2d**) was employed, 2-(phenylseleno)-1-octene was also produced in 18% yield (entry 5). It must be noted that, in the case of R^2 = C_6H_4-OMe-4, *Z*-(*n*-C_6H_{13})(R^1Se)C=C(H)C(O)(R^2) (R^1 = Ph, **5a**; R^1 = C_6H_4OMe-*p*, **5b**), the products of *aroylselenation*,[8] were also produced in 11% and 9% yields, respectively. The *vinylselenation* took place with use of **2h** and **2i** to give the corresponding dienes albeit in low yields (entries 9 and 10). On the other hand, the selenoester with *t*-Bu as R^2 was totally ineffective (entry 11).

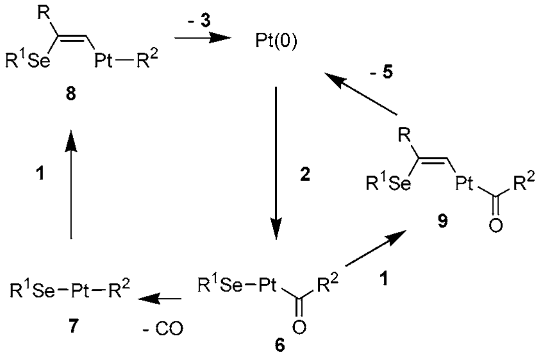
The results of reactions of some alkynes (**1**) with **2a** are summarized in Table 2. The functionalities such as $PhCH_2$−, HO−, and NC− were tolerant toward the arylselenation of **2a** (entries 1−4). The reaction employing phenylacetylene (**1f**) formed **5c** in 19% yield together with 61% (*E*/*Z* = 10/90) of **3o** (entry 5) and the yield of **5** was increased by introducing 4-MeO in the phenyl group to furnish **5d** in 31% yield (entry 6). Then, to anticipate the increment of the formation of **5**, some reactions of **1g** with **2f** were next examined. As a result, the reaction performed under 10 kg/cm^2 of CO afforded **5e** in 42% yield with a trace amount of **3q** (<1%) (Scheme 2).

Scheme 2



A possible mechanism for the present carboselenation of **1** by **2** is shown in Scheme 3 (PPh_3 omitted). The oxidative addition of the Se−C bond of **2** to Pt(0) would trigger the reaction to give Pt(SeR^1)[C(O)R^2] (**6**). The following decarbonylation produced R^1Se−Pt−R^2 (**7**) and then stereo- and regioselective insertion of **1** into the Se−Pt bond would furnish vinyl platinum **8**,[9] making the *C*−*C* bond-forming reductive elimination from Pt(II) possible to afford **3** with

Scheme 3. A Possible Reaction Pathway for the Pt-Catalyzed Carboselenation of **1** (PPh_3 Omitted)



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(8) The aroylselenation of alkyne by selenoester through the Cu-catalyzed Sonogashira-type coupling and subsequent addition of in situ generated selenol to α,β-alkynone are known. Zhao, C. Q.; Huang, X.; Meng, J. B. *Tetrahedron Lett.* **1998**, *39*, 1933.

regeneration of Pt(0).[10] If **1** inserted into the Se−Pt bond of **6** prior to the decarbonylation and then reductive elimination occurred from the resultant vinyl platinum **9**, **5** would be obtained.

In conclusion, this study substantiated that the strategy for arylthiolation of **1** shown in Scheme 1 ($Y = SR^1$) also can be successfully applied to arylselenation ($Y = SeR^1$), providing a new entry for the facile preparation of functionalized vinylselenides.[11] Furthermore, the possibility of aroylselenation was also implicated.

Acknowledgment. The authors gratefully acknowledge the support for this work by a Grant-in-aid for Scientific Research, Ministry of Education, Culture, Sports, Science and Technology of Japan. 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.

Supporting Information Available: Synthetic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The insertion of **1** into the Se−Pt bond also can be involved in Pt-catalyzed hydroselenation of **1**. Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Sonoda, N. *Tetrahedron Lett*. **1992**, *33*, 5525.

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(11) As to the synthetic utility of vinylselenides, see: (a) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373. (b) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, UK, 1986. (c) Yamazaki, S. *Rev. Heteroatom Chem.* **1999**, *21*, 43.