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The First Platinum(0)-Catalyzed Regio- and Stereoselective Thiosilylation of Alkynes Using Disulfides and Disilanes: A New Strategy for Introducing Two Different Heteroatoms into Carbon−Carbon Unsaturated Bonds

Li-Biao Han and Masato Tanaka*

National Institute of Materials and Chemical Research
Tsukuba, Ibaraki 305-8565, Japan

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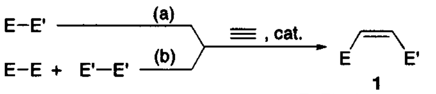
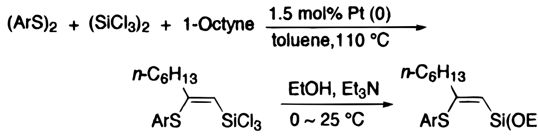
The chemistry for efficient construction of carbon−heteroatom bonds by transition metal catalyzed addition of heteroatom compounds to carbon−carbon unsaturated bonds is emerging rapidly.[1] Particularly interesting and challenging in this category are those involving the regio- and stereoselective simultaneous introductions of two different heteroatoms (E, E′, E ≠ E′; Scheme 1), which enable versatile and elegant synthetic elaborations of the adducts (**1**). However, all of the few reactions reported to date[2] have been performed by adopting the same protocol, using directly the corresponding unsymmetrical E−E′ as reagents (path a), in which a troublesome and time-consuming preparation of the E−E′ linkage can be a serious drawback. On the other hand, related symmetrical compounds (E−E and E′−E′) are generally more accessible and easy to handle. Herein reported is a new protocol for the synthesis of **1** by employing a mixture of two symmetrical heteroatom compounds (path b); heating a mixture of disulfides, disilanes, and alkynes in the presence of a platinum catalyst realizes regio- and stereoselective thiosilylation of alkynes, which readily affords synthetically versatile (*Z*)-1-silyl-2-thio-1-alkenes in good yields.[3,4] This thiosilylation reaction also appears to represent the first metal-catalyzed addition of the group 14 element−chalcogen bond to unsaturated hydrocarbons with high efficiencies.[5]

Scheme 1



1
E, E′ = heteroatom

In a typical experiment, heating a mixture of (4-$ClC_6H_4S)_2$ (1.5 mmol, 430.8 mg), $(SiCl_3)_2$ (1.5 mmol, 403.3 mg), and 1-octyne (3.0 mmol, 330.6 mg) in toluene (3 mL) in the presence of Pt(CH_2=CH_2)($PPh_3)_2$ (34 mg, 1.5 mol % relative to sulfur) at 110 °C for 6 h resulted in complete disappearance of 1-octyne as confirmed by GC.[6] Subsequent additions of Et_3N (10 mmol, 1.4 mL) and EtOH (10 mmol, 0.6 mL) to the reaction mixture followed by purification by column chromatography on silica gel (hexane/ether/Et_3N = 100/10/1) afforded analytically pure (*Z*)-1-(triethoxysilyl)-2-(4′-chlorophenylthio)-1-octene (**2c**) regio- and stereoselectively as pale yellow oil in 83% yield (1.04 g, 2.5 mmol) (eq 1). Surprising is the lack of addition of the disulfide to the alkyne since such an addition reaction is known to proceed in the presence of complex catalysts.[5b] The possible regio- and stereoisomers of **2c** were not formed either.[7,8]



(1)

1a, Ar = Ph; **1b**, Ar = 4-MeC_6H_4; **1c**, Ar = 4-ClC_6H_4 **2c**, Ar = 4-ClC_6H_4, 83%

As demonstrated in Table 1, the platinum-catalyzed thiosilylation could be readily applied to other terminal alkynes, yielding the corresponding (*Z*)-1-silyl-2-thio-1-alkenes (**2**) in good yields with excellent regio- and stereoselectivities. Besides 1-octyne, the reaction of 3-phenyl-1-propyne and other functionalized aliphatic alkynes such as those having chloro, cyano, siloxy, and alkoxycarbonyl groups[9] also proceeded efficiently affording the adducts in high yields. Multiple silyl and thio groups could be easily introduced regio- and stereoselectively to acetylenes having more than one C−C triple bond. For example, the thiosilylation of 1,8-nonadiyne using 1.1 equiv of the disulfide and $(SiCl_3)_2$ gave the corresponding product in 69% yield. Aromatic alkynes such as phenylacetylene, 1-chloro-4-ethynylbenzene, and 4-ethynyltoluene also reacted similarly and good yields of the thiosilylation products were obtained. In contrast to alkynes, alkenes were inert toward the reaction. Consequently, only an adduct through the addition to the triple bond was obtained from 1-ethynylcyclohexene.[10]

Mechanistic investigations revealed that a novel platinum-catalyzed disproportionation reaction of a disulfide $(ArS)_2$ with

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[1] (a) 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. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; John Wiley & Sons: New York, 1992; pp 25−50. (c) *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon Press: Oxford, UK, 1992.

[2] Representative E−E′ additions: (Si−Sn) (a) Mitchell, T. N.; Schneider, U. *J. Organomet. Chem.* **1991**, *407*, 319 and references therein. (B−S) (b) Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219. (Si−Se, Ge−S, and Ge−Se) (c) Tsumuraya, T.; Ando, W. *Organometallics* **1989**, *8*, 2286. (d) Ogawa, A.; Sonoda, N. *Yuki Gosei Kagaku Kyokaishi* (*J. Synth. Org. Chem. Jpn.*) **1993**, *51*, 815. (P−Se) (e) Han, L.-B.; Choi, N.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 7000. (B−Sn) (f) Onozawa, S.-y.; Hatanaka, Y.; Choi, N.; Tanaka, M. *Organometallics* **1997**, *16*, 5389. (B−Si) (g) Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229. (h) Suginome, M.; Nakamura, H.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516. For other relevant studies, see: (i) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713 and references therein.

[3] Conventional synthesis of 1-silyl-2-thioalkenes via radical addition of ArSH to ethynylsilanes: (a) Komarov, N. V.; Torosh, O. G. *Izv. Akad. Nauk SSSR Ser. Khim.* **1967**, *3*, 690. Via cross-coupling of bromoalkenylsilanes with $PhSSnR_3$: (b) Carpita, A.; Rossi, R., Scamuzzi, B. *Tetrahedron Lett.* **1989**, *30*, 2699. Other methods: (c) Hase, T. A.; Lahtinen, L. *J. Organomet. Chem.* **1982**, *240*, 9. (d) Chou, S.-S. P.; Chao, M.-H. *Tetrahedron Lett.* **1995**, *36*, 8825.

[4] For applications in cyclopentenone annulations, see: (a) Magnus, P.; Quagliato, D. *J. Org. Chem.* **1985**, *50*, 1621. Vinylsilanes and vinyl sulfides are useful synthetic intermediates. For vinylsilanes: (b) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. For vinyl sulfides, see ref 4a and references therein.

[5] Palladium-catalyzed additions of strained thia- and selenadigermiranes to acetylene and $PhSeSiMe_3$ to phenylacetylene have been briefly described in refs 2c and 2d. For related pioneering studies, see: (a) Ogawa, A.; Takeba, M.; Kawakami, J.-i, Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1995**, *117*, 7564. (b) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.

[6] The 2-(arylthio)-1-(trichlorosilyl)-1-alkenes (**1**) could be isolated by Kugelrohr distillation, e.g., **1a** in 63% yield.

[7] Weak vinylic signals could be found in the ^1H NMR spectrum of the crude reaction mixture. However, they are not due to either other isomers of the major adduct or the adduct of the disulfides but seems due to an entirely different side product derived from one molecule of silyl sulfide and two molecules of alkynes. See the Supporting Information for details.

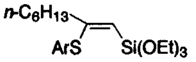
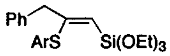
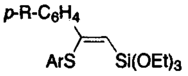
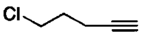
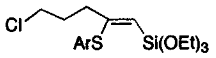
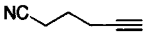
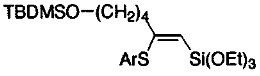
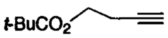
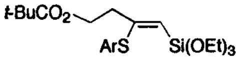
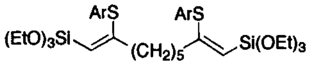
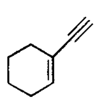
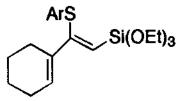
[8] $Pt(PPh_3)_4$ also worked as efficient catalyst to give **2c** in 76% yield. In contrast, complexes such as $Pt(PPh_2Me)_4$, $Pt(cod)_2$, $PtCl_2(PPh_3)_2$, $Pd_2(dba)_3$, $PdCl_2(PhCN)_2$, and $PdCl_2(PPh_3)_2$ did not show any catalytic activity, and an attempted reaction using $Pd(PPh_3)_4$ produced a rather complicated result. Among disulfides screened for the reaction of 1-octyne, (4-$ClC_6H_4S)_2$ gave the highest yield of the adduct (**1c**, 95%), followed by $(PhS)_2$ (**1a**, 65%) and (4-$MeC_6H_4S)_2$ (**1b**, 52%). However, formation of an analogous adduct could not be confirmed in the reaction with (*c*-$C_6H_{11}S)_2$. As for disilane compounds, use of $(SiMe_3)_2$, $(SiClMe_2)_2$, $(SiFMe_2)_2$, $(SiPhMe_2)_2$, or $[Si(OMe)_3]_2$ in place of $(SiCl_3)_2$ did not form the corresponding adducts under similar reaction conditions.

[9] Cleavage of C−O bonds by silyl sulfides is known. See: Armitage, D. A. In *The Silicon−Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1991; pp 213−243.

[10] The relatively low yield was due to rather extensive formation of a side product as described in ref 7.

S0002-7863(98)01474-7 CCC: $15.00

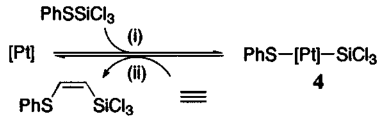
Table 1. Thiosilylation of Terminal Alkynes[a]

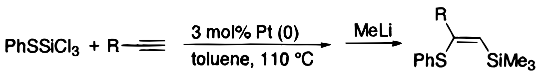
alkyne	adduct[b]		% yield[c]
n-C$_6$H$_{13}$—≡			83
			76
p-R-C$_6$H$_4$—≡		R = H R = Cl R = Me	62 65 60
			79
			81
TBDMSO—(CH$_2$)$_4$—≡			72
			87
≡—(CH$_2$)$_5$—≡ [d]			69
			51

[a] Conditions: (i) Alkyne (3 mmol), $(4\text{-ClC}_6\text{H}_4\text{S})_2$ (1.5 mmol), $(\text{SiCl}_3)_2$ (1.5 mmol), and $\text{Pt(CH}_2\text{=CH}_2)(\text{PPh}_3)_2$ (34 mg) in toluene (3 mL), 110 °C, 6~10 h; (ii) Et_2O (30 mL), Et_3N (10 mmol), EtOH (10 mmol), 0 ~ 25 °C, 1 h. [b] Ar stands for 4-chlorophenyl group. [c] Isolated yields after column chromatography or preparative GPC. [d] 1.4 mmol of the diyne was used.

$(\text{SiCl}_3)_2$ forming ArSSiCl_3 took place rapidly at the very early stage of the addition shown by eq 1. The reaction could be easily monitored by ^{13}C NMR spectroscopy. Thus, when $\text{Pt(CH}_2\text{=CH}_2)(\text{PPh}_3)_2$ (1.5 mol % relative to sulfur) was added to a solution of $(\text{PhS})_2$, and $(\text{SiCl}_3)_2$ in benzene-d_6 at room temperature, it immediately began to smell of PhSSiCl_3 and PhSSiCl_3 was formed in approximately 40 and 80% yields after 1.5 and 15 h, respectively.[11] On the other hand, disilanes such as $(\text{SiMe}_3)_2$, which are unreactive in the present thiosilylation reaction,[8] do not undergo the disproportionation to generate silyl sulfides. Accordingly the thiosilylation is envisioned to proceed via oxidative addition of ArSSiCl_3 to Pt to form **4** having a S–Pt–Si linkage,[12] which reacts with an alkyne (Scheme 2). This proposal was further reinforced by the following two experiments. First, thiosilylation reactions took place when PhSSiCl_3 was employed as the substrate in place of the mixture of $(\text{PhS})_2$ and $(\text{SiCl}_3)_2$ (eq 2). Thus, highly air- and moisture sensitive PhSSiCl_3 of strong stench was prepared by a reaction of PhSLi with a large excess of SiCl_4 in a low (~7%) yield. Upon heating with alkynes in the presence of $\text{Pt(CH}_2\text{=CH}_2)(\text{PPh}_3)_2$, the thiosilylation adducts were obtained in good yields. However, an attempted reaction using PhSSiMe_3 did not work at all. Second, as confirmed by ^{31}P NMR spectroscopy, oxidative addition of PhSSiCl_3 to $\text{Pt(PEt}_3)_3$ readily occurred at room temperature to afford *trans*-$\text{Pt(PhS)(SiCl}_3)(\text{PEt}_3)_2$ (**4a**, δ = 13.5 ppm, J_{PPt} = 2490 Hz) whereas a similar reaction of PhSSiMe_3 did not.[13]

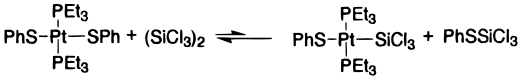
Scheme 2



 (2)

3a, R = n-C$_6$H$_{13}$, 65%
3b, R = Ph, 71%

Interestingly, a reaction of $(\text{SiCl}_3)_2$ with complex **5a** (^{31}P NMR, δ = 12.2 ppm, J_{PPt} = 2511 Hz), prepared via the facile oxidative addition of $(\text{PhS})_2$ to $\text{Pt(PEt}_3)_4$, clearly disclosed that **4a** was in equilibrium with **5a** in the solution (eq 3).[14] Moreover, the equilibrium constant at 23 °C was extremely small to be estimated at only 0.03. This amazingly indicates that species **4** of such a negligible concentration is by far more reactive than **5**, present as the major component in the equilibrium, leading to the selective addition of Si–S rather than S–S.[15]

 (3)

$$\text{PhS-}\overset{\text{PEt}_3}{\underset{\text{PEt}_3}{\text{Pt}}}\text{-SPh} + (\text{SiCl}_3)_2 \rightleftharpoons \text{PhS-}\overset{\text{PEt}_3}{\underset{\text{PEt}_3}{\text{Pt}}}\text{-SiCl}_3 + \text{PhSSiCl}_3 \quad (3)$$

5a **4a**

Extensions of the present strategy to other heteroatom compounds are now under extensive study.

Acknowledgment. We thank the Japan Science and Technology Corporation (JST) for partial financial support through the CREST program.

Supporting Information Available: Text describing experimental details and spectral and/or analytical data of the products (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[11] An elevated temperature accelerated this reaction, e.g., ~85% of PhSSiCl_3 after 2 h at 60 °C. On the other hand, under the same reaction conditions, i.e., at 60 °C, a procedure similar to eq 1 formed **1a** in only ~3% even after 24 h, indicating that the disproportionation reaction is faster than the thiosilylation. In the absence of the platinum catalyst, PhSSiCl_3 was not formed at all even after heating at 80 °C for 3 days.

[12] In view of the disproportionation, the thiosilylation does not entirely proceed through the oxidative addition of preformed PhSSiCl_3, but there is a marginal route (in particular, at the early stages of the reaction) which involves the same S–Pt–Si species **4** directly formed through the disproportionation process between the disulfide and the disilane.

[13] Reaction of PhSSiCl_3 with $\text{Pt(PPh}_3)_3$ also took place easily at room temperature.

[14] For oxidative addition of group 14–chalcogen bonds, see: Han, L.-B.; Shimada, S.; Tanaka, M. *J. Am. Chem. Soc.* **1997**, *119*, 8134.

[15] We tentatively propose that the catalysis involves insertion of an alkyne into the S–Pt (but not Si–Pt) bond of **4**, which is consistent with (a) the strong *trans* influence of the silyl ligand, (b) enhanced bond strength of the Si–Pt bond by introduction of electronegative groups (Cl) to Si, and (c) the regioselectivity of the catalysis that suggests terminal attachment of the bulkier platinum moiety at the insertion stage.