

Palladium(0)-catalyzed regio- and stereoselective addition of heteroatom compounds bearing Si–Se, Ge–Se, and Si–Ge bonds to phenylacetylene

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Received 3 June 1997; received in revised form 29 July 1997

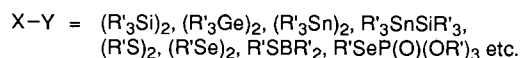
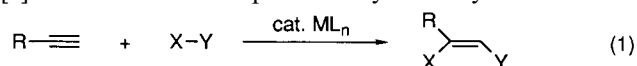
Abstract

A novel palladium(0)-catalyzed addition of a silyl selenide (**1**, Me₃SiSePh) to phenylacetylene proceeds regio- and stereoselectively to give (*Z*)-1-phenylseleno-2(trimethylsilyl)styrene (**2**). Similarly, a germyl selenide (**3**, Me₃GeSePh) adds to phenylacetylene with excellent regio- and stereoselectivity. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Palladium catalyst; Regio- and stereoselective addition; Silyl selenide; Germyl selenide; Silylgermane

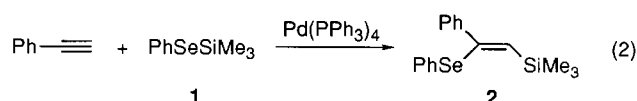
1. Introduction

Transition metal catalyzed addition of heteroatom compounds bearing main group metal–metal bonds to carbon–carbon unsaturated bonds is an interesting and challenging subject in organic chemistry [1]. Along this line, the additions to acetylenes of Group 14 compounds like disilanes [2], distannanes [3], digermanes [4], and silylstannanes [5] have been well documented (Eq. 1). Recently we have discovered that the addition to acetylenes of Group 16 compounds such as disulfides and diselenides (which have been believed to act as a catalyst poison) are successfully catalyzed by transition metal catalysts [6]. Furthermore, transition metal catalyzed addition of compounds with a B–S [7] or P–Se [8] bonds has been reported very recently.



2. Methods

We disclose here the first example of the palladium(0) catalyzed addition of a silyl selenide to phenylacetylene, which provides the styrene derivative with vicinal silyl and selenenyl groups, as indicated in Eq. 2.



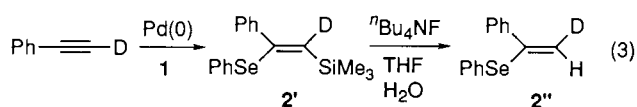
We attempted the preliminary experiments of the reaction of trimethylsilyl phenyl selenide (**1**, Me₃SiSePh) (0.4 mmol) with phenylacetylene (0.6 mmol) in the presence of various transition metal catalysts (5 mol%) at 120°C for 24 h without solvent. Among the catalysts examined, PdCl₂, Pd(PPh₃)₂Cl₂, Pd₂(dba)₃, Ni(PPh₃)₂Cl₂, Ni(PPh₃)₄, Pt(PPh₃)₄, Rh(PPh₃)₃Cl, and [Rh(CO)₂Cl]₂ exhibited no catalytic activity toward the addition of **1** to phenylacetylene. Contrary to this, Pd(PPh₃)₄ and Pd(OAc)₂ worked as catalysts for the desired addition to give (*Z*)-1-phenylseleno-2-(trimethylsilyl)styrene (**2**) [9] regio- and stereose-

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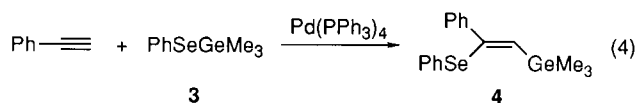
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lectively in 25 and 10% yields, respectively. Similar conditions can be employed with some other aromatic acetylenes (p -X-C₆H₄-C≡CH, X = Me (18%); X = F (13%)); however silylselenation of aliphatic acetylenes like 1-octyne did not proceed at all under similar conditions.

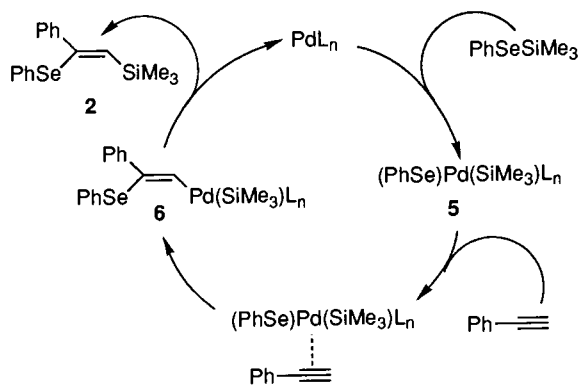
The regio- and stereochemistry of **2** was determined by protodesilylation with ⁿBu₄NF (1 N in THF–H₂O) [10]. After the palladium catalyzed reaction of phenylacetylene-1-D with **1**, the protodesilylation of the adduct (**2'**) with ⁿBu₄NF afforded (*E*)-1-(phenylseleno)styrene-2-D (**2''**) exclusively (Eq. 3) [11].



Similarly, the addition of trimethylgermyl phenyl selenide (**3**) to phenylacetylene at 120°C for 12 h was also catalyzed by Pd(PPh₃)₄, giving (*Z*)-1-phenylseleno-2-(trimethylgermyl)styrene (**4**) [12] in 35% yield (Eq. 4) ([4c]). The procedure was readily applied to some other aromatic acetylenes (p -X-C₆H₄-C≡CH, X = Me (23%); X = F (20%)).

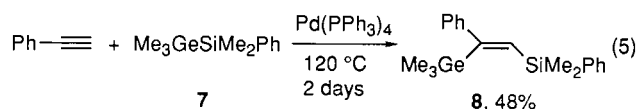


Although it may be premature to discuss the reaction mechanism, a possible reaction pathway for the addition of the silyl selenide to phenylacetylene is shown in Scheme 1. The first step may be the oxidative addition of PhSeSiMe₃ to a low valent palladium to generate 'PhSe[Pd]SiMe₃L₂' (**5**) [13–15]. Regio- and stereoselective selenopalladation of **5** to phenylacetylene provides a vinylic palladium species (**6**), followed by reductive elimination of the product (**2**) with the regeneration of the catalyst [16].



Scheme 1.

As an extension of our interest in the transition metal catalyzed additions to acetylenes of analogous compounds bearing a heteroatom–heteroatom bond, we examined the reaction of a silylgermane, a silyl sulfide, and a silyl telluride. Unfortunately, a silyl sulfide (PhSSiMe₃) and a silyl telluride (PhTeSiMe₃) did not give the desired addition product under similar conditions (most of the starting materials was recovered). However, the addition of a silylgermane (**7**, Me₃GeSiMe₂Ph) to phenylacetylene took place successfully by using Pd(PPh₃)₄ as a catalyst (Eq. 5) [12,17,18].

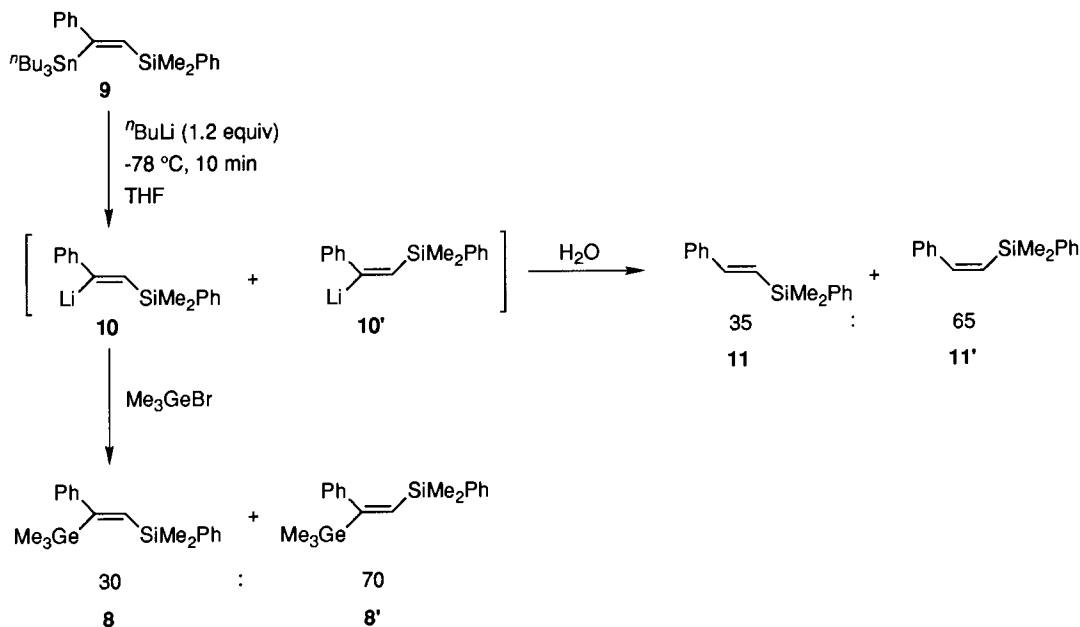


The regio- and stereochemistry of the adduct **8** was determined as follows (Scheme 2). Since silylstannanes were known to add to terminal acetylenes regio- and stereoselectively [5], we prepared 1-(tributylstannyl)-2-(dimethylphenylsilyl)styrene (**9**) from ⁿBu₃SnSiMe₂Ph and phenylacetylene. The tin–lithium exchange reaction of **9** with ⁿBuLi generated vinylic lithiums (**10** and **10'**) in the ratio of 35:65 (estimated based on the ratio of the vinylic silanes (**11** and **11'**) formed by the protonation of **10** and **10'**) ([5a]). The capturing of **10** and **10'** with Me₃GeBr provided a stereoisomeric mixture of 1-(trimethylgermyl)-2-(dimethylphenylsilyl)styrene (**8** and **8'**) in the ratio of 30:70. The minor isomer could be identified as the product (**8**) obtained by the palladium(0) catalyzed reaction of **7** with phenylacetylene.

In conclusion, the additions of a silyl selenide, a germlyl selenide, and a silylgermane to phenylacetylene have been discovered to be catalyzed by palladium complexes like Pd(PPh₃)₄. These additions proceed with excellent regio- and stereoselectivity, giving vicinal bifunctionalized styrenes. Further studies on the scope and limitation of the transition metal catalyzed addition of Group 14 and 16 element compounds to carbon–carbon unsaturated bonds are currently under investigation.

Acknowledgements

This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (No. 09239102) from the Ministry of Education, Science and Culture, 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.



Scheme 2.

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