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Journal of Organometallic Chemistry 564 (1998) 1–4

Journal of Organometallic Chemistry

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

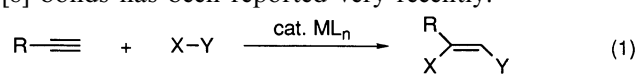
Abstract

A novel palladium(0)-catalyzed addition of a silyl selenide (**1**, $Me_3SiSePh$) to phenylacetylene proceeds regio- and stereoselectively to give (*Z*)-1-phenylseleno-2(trimethylsilyl)styrene (**2**). Similarly, a germyl selenide (**3**, $Me_3GeSePh$) 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.



(1)

X–Y = $(R'_3Si)_2$, $(R'_3Ge)_2$, $(R'_3Sn)_2$, $R'_3SnSiR'_3$, $(R'S)_2$, $(R'Se)_2$, $R'SBR'_2$, $R'SeP(O)(OR')_3$ etc.

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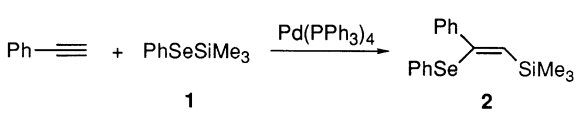
2. Methods

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.



1 **2** (2)

We attempted the preliminary experiments of the reaction of trimethylsilyl phenyl selenide (**1**, $Me_3SiSePh$) (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, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd_2(dba)_3$, $Ni(PPh_3)_2Cl_2$, $Ni(PPh_3)_4$, $Pt(PPh_3)_4$, $Rh(PPh_3)_3Cl$, and $[Rh(CO)_2Cl]_2$ exhibited no catalytic activity toward the addition of **1** to phenylacetylene. Contrary to this, $Pd(PPh_3)_4$ and $Pd(OAc)_2$ worked as catalysts for the desired addition to give (*Z*)-l-phenylseleno-2-(trimethylsilyl)styrene (**2**) [9] regio- and stereose-

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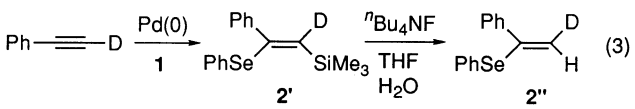
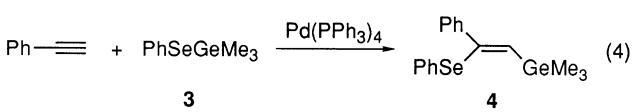
lectively in 25 and 10% yields, respectively. Similar conditions can be employed with some other aromatic acetylenes (p-X–C_6H_4–C≡CH, X = Me (18%); X = F (13%)); however silylselenation of aliphatic acetylenes like 1-octyne did not proceed at all under similar conditions.

The regio- and stereochemistry of **2** was determined by protodesilylation with $^nBu_4NF$ (1 N in THF–H_2O) [10]. After the palladium catalyzed reaction of phenylacetylene-1-D with **1**, the protodesilylation of the adduct (**2′**) with $^nBu_4NF$ afforded (*E*)-1-(phenylseleno)styrene-2-D (**2″**) exclusively (Eq. 3) [11].



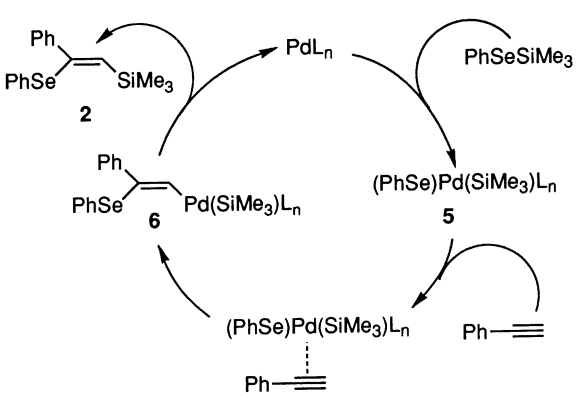
(3)

Similarly, the addition of trimethylgermyl phenyl selenide (**3**) to phenylacetylene at 120°C for 12 h was also catalyzed by $Pd(PPh_3)_4$, giving (*Z*)-1-phenylseleno-2-(trimethylgermyl)styrene (**4**) [12] in 35% yield (Eq. 4) ([4]c). The procedure was readily applied to some other aromatic acetylenes (p-X–C_6H_4–C≡CH, X = Me (23%); X = F (20%)).



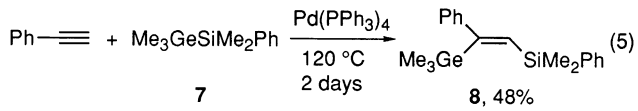
(4)

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 $PhSeSiMe_3$ to a low valent palladium to generate 'PhSe[Pd]$SiMe_3L_2$' (**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 ($PhSSiMe_3$) and a silyl telluride ($PhTeSiMe_3$) did not give the desired addition product under similar conditions (most of the starting materials was recovered). However, the addition of a silylgermane (**7**, $Me_3GeSiMe_2Ph$) to phenylacetylene took place successfully by using $Pd(PPh_3)_4$ as a catalyst (Eq. 5) [12,17,18].



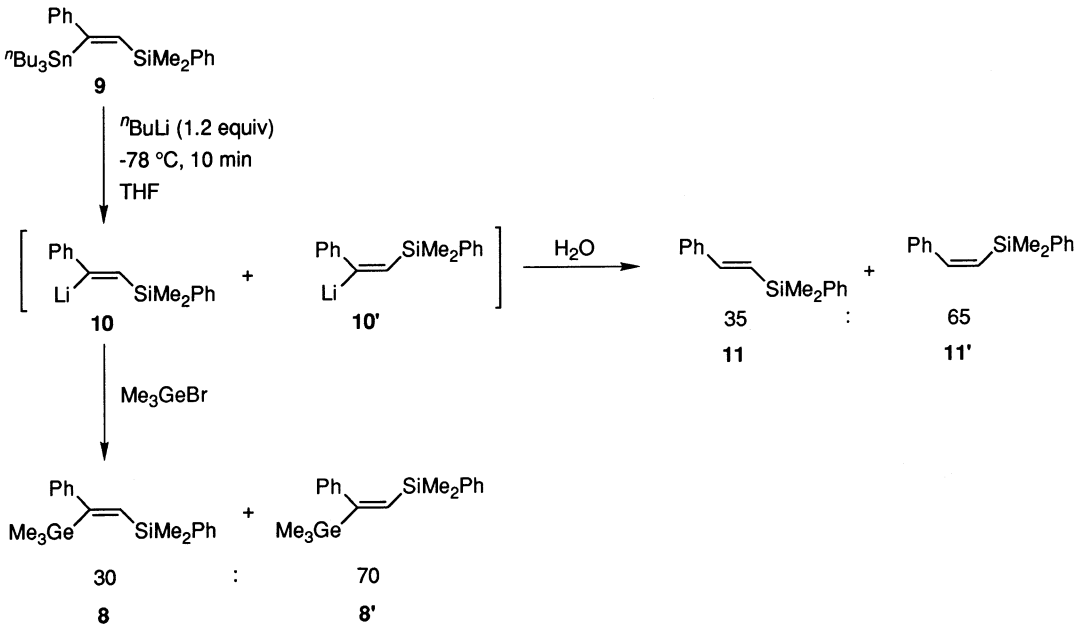
(5)

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 $^nBu_3SnSiMe_2Ph$ and phenylacetylene. The tin–lithium exchange reaction of **9** with ^{n}BuLi 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′**) ([5]a). The capturing of **10** and **10′** with Me_3GeBr 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 germyl selenide, and a silylgermane to phenylacetylene have been discovered to be catalyzed by palladium complexes like $Pd(PPh_3)_4$. 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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[9] Representative procedure for the Pd(0) catalyzed addition to phenylacetylene: in a glass tube (ϕ 1.2 cm, 110 cm) were added, under argon atmosphere, phenyl trimethylsilyl selenide (770 mg, 3.36 mmol), phenylacetylene (588 mg, 5.75 mmol), and tetrakis(triphenylphosphine)palladium (174 mg, 5 mol%), the tube was then sealed under reduced pressure. After the mixture was heated at 120°C for 15 h, the resulting mixture was filtered through Celite. The filtrate was diluted with 50 ml of Et_2O/MeOH (8/2), and the solution was washed with aqueous NaOH, and then saturated NaCl (aq.). The extract was dried over $MgSO_4$, and concentrated under reduced pressure. Purification by preparative TLC (silica gel, hexane as an eluent) provided (*Z*)-1 phenylseleno-2-(trimethylsilyl)styrene (**2**): oil; ^{1}H-NMR (270 MHz, $CDCl_3$): δ 0.27 (s, 9H), 6.68 (s, 1H), 7.05–7.53 (m, 10H); ^{13}C-NMR (68 MHz, $CDCl_3$): δ −0.50, 126.27, 127.88, 127.88, 128.77, 131.41, 131.46, 140.69; MS (EI) *m*/*e* 332 (M^+, 1.4); Anal. Calc. for $C_{17}H_{20}SeSi$: C, 61.62; H, 6.08. Found: C, 61.89; H, 6.01.

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