COMMUNICATION

ChemComm
www.rsc.org/chemcomm

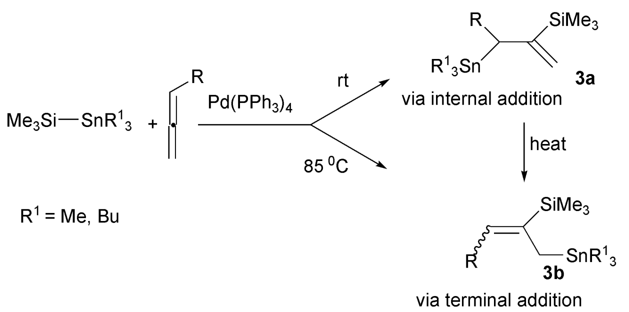
Highly regio- and stereoselective silylstannation of allenes catalyzed by phosphine-free palladium complexes†

Masilamani Jeganmohan, Muthian Shanmugasundaram, Kuo-Jui Chang and Chien-Hong Cheng*
Department of Chemistry, Tsing Hua University, Hsinchu, Taiwan 300. E-mail: chcheng@mx.nthu.edu.tw; Fax: +886-3-5724698; Tel: +886-3-5721454

Received (in Cambridge, UK) 4th July 2002, Accepted 16th September 2002
First published as an Advance Article on the web 1st October 2002

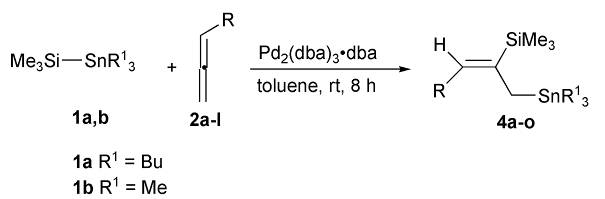
The addition reaction of silylstannanes with allenes in the presence of $Pd_2(dba)_3$·dba in toluene affords (*E*)-alkenylsilanes having an allylstannane moiety exclusively in good to excellent yields.

The addition of main group metal–metal bonds such as Si–Si, Sn–Sn, Si–Sn, Ge–Sn, B–Si, B–B bonds to allenes is a powerful strategy for the construction of organometallic compounds having both vinylic and allylic metal moieties that are versatile synthetic reagents in organic synthesis.[1,2] Though the silylstannation of allenes catalyzed by $Pd(PPh_3)_4$ is known, the observed regio- and stereoselectivity was poor (Scheme 1).[3,4] The initial kinetic product **3a** undergoes 1,3-shift of the stannyl moiety upon heating to give a mixture of *E*/*Z* isomers **3b**. Recent effort in our laboratories revealed that phosphine-free palladium complexes effectively catalyzed three-component coupling reactions of allenes.[5] These observations and our interest in metal-mediated allene chemistry[5,6] promoted us to explore the reaction of silylstannane with allenes in the presence of phosphine-free palladium complexes. Herein, we wish to report a highly regio- and stereoselective addition of silylstannanes to allenes by using phosphine-free palladium complexes as catalysts to give (*E*)-alkenylsilanes having an allylstannane moiety in high yields.



Scheme 1

The addition reaction of trimethyl(tributylstannyl)silane **1a** with phenylallene **2a** in the presence of $Pd_2(dba)_3$·dba (5 mol%) (dba = dibenzylideneacetone) in toluene at ambient temperature proceeded quantitatively to give an allylstannane derivative **4a** (Scheme 2). No other regioisomer or stereoisomer other than **4a** was detected in the ^{1}H NMR spectrum of the crude reaction mixture. Control experiments revealed that in the absence of palladium catalysts, no reaction occurred. The catalytic reaction is highly regioselective with the silyl group adding to the middle carbon and the stannyl group adding to the unsubstituted terminal carbon of **2a**. The structure of **4a** was ascertained by ^{1}H and ^{13}C NMR and mass spectral data. The stereochemistry of **4a** was unequivocally established by typical ^{1}H NMR NOE techniques.



Scheme 2

To understand the effect of catalyst, several phosphine-free palladium catalysts were tested. All these complexes $PdCl_2$, $Pd(acac)_2$, $Pd(OAc)_2$, $PdCl_2(PhCN)_2$ and $PdCl_2(CH_3CN)_2$ in toluene are lower in catalytic activity relative to $Pd_2(dba)_3$·dba for the addition of **1a** to allene **2a** affording **4a** in 70, 65, 61, 23 and 20% yields, respectively. Examination of the influence of solvent on the catalytic activity revealed that toluene was the solvent of choice. Other solvents such as EA, CH_2Cl_2 and THF were also effective, giving **4a** in 88, 85 and 73% yields, respectively. Coordinating solvents CH_3CN or DMF were less suitable for the present catalytic reaction furnishing **4a** in 27 and 19% yields, respectively. The same reaction when carried out at 80 °C in the presence of $Pd_2(dba)_3$·dba in toluene proceeded quantitatively to afford single product **4a**.

Table 1 delineates the results obtained for the reaction of silylstannanes **1a,b** with allenes **2a**–**l**. Aryl allenes with an electron-withdrawing or an electron-donating group on the aromatic ring react efficiently with **1a** to give the corresponding allylstannanes **4b**–**f** in high yields indicating that this catalytic reaction is insensitive to electronic effects (entries 2–6). Similarly, the addition is also insensitive to steric substituents. 1-Naphthylallene **2g** and *tert*-butylallene **2h** having a bulky group react smoothly with **1a** to afford the corresponding products **4g** and **4h** in 82 and 80% yields (entries 7 and 8).

Table 1 Results of palladium-catalyzed addition of silylstannane (**1**) with allene (**2**)[a]

Entry	1	R¹	2	R	Product	E/Z	Yield[b] (%)
1	**1a**	-Bu	**2a**	$-C_6H_5$	**4a**	> 99	91 (99)
2	**1a**	-Bu	**2b**	2-Me-phenyl	**4b**	> 99	82
3	**1a**	-Bu	**2c**	3-Me-phenyl	**4c**	> 99	91
4	**1a**	-Bu	**2d**	4-OMe-phenyl	**4d**	> 99	90
5	**1a**	-Bu	**2e**	4-Br-phenyl	**4e**	> 99	89
6	**1a**	-Bu	**2f**	4-$COCH_3$-phenyl	**4f**	> 99	88
7	**1a**	-Bu	**2g**	1-naphthyl	**4g**	> 99	82
8	**1a**	-Bu	**2h**	*tert*-butyl	**4h**	> 99	80
9	**1a**	-Bu	**2i**	*n*-butyl	**4i**	> 99	90 (96)
10	**1a**	-Bu	**2j**	*n*-octyl	**4j**	> 99	85
11	**1a**	-Bu	**2k**	cyclopentyl	**4k**	> 99	87
12	**1a**	-Bu	**2l**	cyclohexyl	**4l**	> 99	88 (95)
13	**1b**	-Me	**2a**	$-C_6H_5$	**4m**	> 99	90
14	**1b**	-Me	**2h**	*tert*-butyl	**4n**	> 99	83
15	**1b**	-Me	**2i**	*n*-butyl	**4o**	> 99	87

[a] The reaction of silylstannane (1.00 mmol) with allene (1.30 mmol) was carried out at rt for 8 h in toluene (2.0 ml) and $Pd_2(dba)_3$·dba (5 mol%). [b] Isolated yields; yields in the parentheses were measured from the crude products by the ^{1}H NMR integration method using mesitylene as an internal standard.

† Electronic supplementary information (ESI) available: synthesis and characterization of compounds **4**. See http://www.rsc.org/suppdata/cc/b2/b206488j/

DOI: 10.1039/b206488j

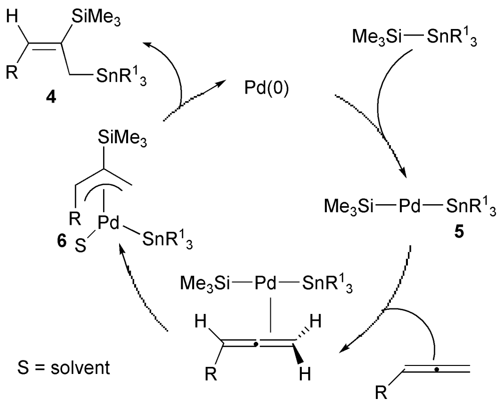
Under similar reaction conditions, the addition reaction of aliphatic allenes *n*-butylallene **2i**, *n*-octylallene **2j**, cyclopentylallene **2k** and cyclohexylallene **2l** with **1a** also proceeds smoothly to give the corresponding allylstannanes **4i–l** in high yields (entries 9–12).

The catalytic addition can be extended to trimethyl(trimethylstannyl)silane **1b**. Thus, the reaction of **1b** with **2a**, **2h** and **2i** gave the corresponding silylstannation products **4m–o** in 90, 83 and 87% yields. The reaction is highly regio- and stereoselective affording (*E*)-alkenylsilanes having an allylstannane moiety exclusively in all of these reactions (Table 1).

Comparison of the present results with those reported previously[3,4] reveals marked difference between these two catalytic reactions. First, for the present $Pd_2(dba)_3$·dba catalyzed silylstannation, the reaction is highly regioselective, with the stannyl group always connecting to the unsubstituted terminal carbon of the allene moiety, irrespective of the substituent on the silylstannane and allene moieties. This is in sharp contrast to the reported reaction using $Pd(PPh_3)_4$ as the catalyst giving initially kinetic product **3a** with the stannyl group attaching to the substituted terminal carbon of the allene group. The latter then undergoing 1,3-shift of the stannyl group to regioisomer **3b** with the stannyl group attached to the unsubstituted terminal carbon of the allene moiety. The ratio of the regioisomers was highly influenced by the substituents on both the allene and silylstannane moieties. Secondly, only *E* stereoselectivity of the reaction products **4** was observed for the present catalytic reaction, but a mixture of *E* and *Z* isomeric products **3b** was isolated for the reported reaction.

Based on the known palladium chemistry, a mechanism involving face-selective coordination of allene to the palladium center is proposed to account for the observed regio- and stereochemistry of products (Scheme 3). The catalytic reaction is likely initiated by the oxidative addition of silylstannane to Pd(0) to give Pd(II) intermediate **5**.[7] The terminal double bond of allene is then coordinated favorably to the palladium center of **5** at the face opposite to the substituents **R** to avoid steric congestion. Insertion of the coordinated double bond of allene to the Pd–Si bond affords π-allyl palladium complex **6** with the R group anti to the $SiMe_3$ moiety on the allyl group. Subsequent reductive elimination of **6** gives the desired product **4** and regenerates the Pd(0) catalyst. The anti form of **6** is solely responsible for the exclusive formation of (*E*)-vinylsilane derivatives **4**.

In summary, a highly regio- and stereoselective silylstannation of allenes has been demonstrated using phosphine-free palladium complexes as catalysts. The nature of the ligands on palladium complexes influences tremendously the regio- and stereochemistry of the reaction. The vinylsilane and allylstannane moieties present in these products allow a large variety of chemical modifications. Further work is in progress to study the application of these products.



Scheme 3

We thank the National Science Council of the Republic of China (NSC 90-2811-M-007-034) for the support of this research.

Notes and references

1 (*a*) For the applications of alkenyl- and allyl-metals in organic synthesis, see *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone, G. Wilkinson and A. McKillop, Pergamon, Oxford, 1995, vol. 11; (*b*) R. Zimmer, C. U. Dinesh, E. Nandanam and F. A. Khan, *Chem. Rev.*, 2000, **100**, 3067.

2 (*a*) H. Watanabe, M. Saito, N. Sutou, K. Kishimoto, J. Inose and Y. Nagai, *J. Organomet. Chem.*, 1982, **225**, 343; (*b*) T. N. Mitchell, U. Schneider and B. Frohling, *J. Organomet. Chem.*, 1990, **384**, C53; (*c*) S-y Onozawa, Y. Hatanaka and M. Tanaka, *Chem. Commun.*, 1999, 1863; (*d*) M. Suginome, Y. Ohmori and Y. Ito, *Synlett*, 1999, 1567; (*e*) F.-Y. Yang and C.-H. Cheng, *J. Am. Chem. Soc.*, 2001, **123**, 761.

3 T. N. Mitchell, H. Killing, R. Dicke and R. Wickenkamp, *J. Chem. Soc. Chem. Commun.*, 1985, 354.

4 T. N. Mitchell and U. Schneider, *J. Organomet. Chem.*, 1991, **407**, 319.

5 (*a*) M.-Y. Wu, F.-Y. Yang and C.-H. Cheng, *J. Org. Chem.*, 1999, **64**, 2471; (*b*) F.-Y. Yang, M.-Y. Wu and C.-H. Cheng, *Tetrahedron Lett.*, 1999, **40**, 6055; (*c*) F.-Y. Yang, M.-Y. Wu and C.-H. Cheng, *J. Am. Chem. Soc.*, 2000, **122**, 7122; (*d*) T.-H. Huang, H.-M. Chang, M.-Y. Wu and C.-H. Cheng, *J. Org. Chem.*, 2002, **67**, 99.

6 (*a*) H.-M. Chang and C.-H. Cheng, *J. Org. Chem.*, 2000, **65**, 1767; (*b*) H.-M. Chang and C.-H. Cheng, *Org. Lett.*, 2000, **2**, 3349.

7 S.-K. Kang, Y.-H. Ha, B.-S. Ko, Y. Lim and J. Jung, *Angew. Chem., Int. Ed.*, 2002, **41**, 343.