APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 65–67
Materials, Nanoscience and Catalysis **AOC**

Short communication

An alternative and effective catalyst for the silastannation of arylacetylenes with $Me_3SiSnBu_3$ at room temperature

Taichi Nakano[1]*, Takashi Miyamoto[1], Takanori Endoh[1], Makoto Shimotani[1], Naoki Ashida[1], Toshishige Morioka[1] and Yutaka Takahashi[2]

[1]Department of Material Science and Technology, School of High-Technology for Human Welfare, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0395, Japan
[2]Analytical Instrument Division, JEOL, Ltd, 1-2 Musashino, 3-chome Akishima, Tokyo 196-8558, Japan

Received 1 September 2003; Revised 6 September 2003; Accepted 7 September 2003

The palladium-catalyzed silastannation of acetylenes with tributyl(trimethylsilyl)stannane in the presence of triethylphosphite is reported for the first time. The reaction occurs at room temperature to give (*Z*)-silyl(stannyl)ethenes in high yields. The protodemetallation of the resulting adducts with HCl–tetraethylammonium chloride is described first, which demonstrates that the reaction is governed only by the stability of a carbonium ion arising from the protonation to (*Z*)-silyl(stannyl)ethenes rather than the hard and soft acid and base principle, i.e. the β-cation stabilization effect ($\sigma-\pi$ stabilization one) of a stannyl group in the carbonium ion is rather significant. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: palladium catalysis; silastannation; (*Z*)-silyl(stannyl)ethenes; selective demetallation; $\sigma-\pi$ stabilization effect; (*E*)-1-aryl-2-silylethenes

vic-Silyl(stannyl)ethenes are fascinating and versatile building blocks for constructing many characteristic organic molecules by organic transformation involving the Migita–Kosugi–Stille reaction.[1–3] Therefore, much effort has been directed to the synthesis of *vic*-silyl(stannyl)ethenes.[4,5] The silastannation of acetylenes is one of the candidates for this objective. The addition has been reported to occur, in many cases, both regio- and stereo-selectively in the presence of tetrakis(triphenylphosphine)palladium(0) to give (*Z*)-silyl(stannyl)ethenes. Thus, Mitchell and co-workers[6,7] reported the reaction of several terminal acetylenes using trimethyl(trimethylsilyl)stannane, which was conducted at 60–70 °C without solvent. Chenard and co-workers[8–10] also reported the reaction of acetylenes including phenylacetylene using (t-butyldimethylsilyl)trimethylstannane at 65 °C in tetrahydrofuran (THF). The catalysis was completed within 4–8 h to give the expected (*Z*)-silyl(stannyl)ethenes in 10–90% yields. Ritter[11] applied silastannation for the synthesis of stereodefined stannylethenes. Mori and co-workers[12,13] examined the protodemetallation of (*Z*)-silyl(stannyl)ethenes, obtained by the silastannation of 1-alkynes, using hydroiodic acid.[12] All these silastannations required elevated temperature reaction conditions. On the other hand, Ito and co-workers[14] recently reported the $Pd(OAc)_2$–t-octyl isonitrile combination system catalyzing the silastannation of acetylenes using (t-butyldimethylsilyl)trimethylstannane at room temperature. However, the catalysis needs a large amount of the expensive t-octyl isonitrile ligand for the larger scale synthesis. In terms of the importance of the (*Z*)-silyl(stannyl)ethenes and economic benefit, an alternative and inexpensive ligand is required. We found for the first time that a phosphite is the best alternative choice for the silastannation. We now report the preliminary results for the $Pd(dba)_2$–$2P(OEt)_3$-catalyzed silastannation of arylacetylenes occurring at room temperature. In addition, we would like to present here the first conclusive experimental results for the governing factor for

*Correspondence to: Taichi Nakano, Department of Material Science and Technology, School of High-Technology for Human Welfare, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0395, Japan.
E-mail: naka1214@wing.ncc.u-tokai.ac.jp

the protodemetallation of silyl(stannyl)ethenes, which can be used in the protodemetallation of silyl(stannyl)ethenes with the HCl–tetraethylammonium chloride combination, the hard and soft acid and base (HSAB) principle[12,15] or the $\sigma-\pi$ stabilization effect[16–18] of the Group 14 elements (tin or silicon).

The silastannation of arylacetylenes was first examined in dry THF using a 2:1 mixture of phenylacetylene and the silylstannane **1** in the presence of 1 mol% of $Pd(dba)_2$ and 2 mol% of triethylphosphite based on the silylstannane **1** (Scheme 1). The reaction occurred at room temperature and was completed in 1.5 h. Column chromatography of the resulting mixture gave (*Z*)-1-(tributylstannyl)-2-(trimethylsilyl)-1-phenylethene **(2a)** in 70% yield, the structure of which was identified from the NMR data. The NMR coupling constants between tin and the vinylic proton (158.8 Hz for ^{117}Sn and 166.0 Hz for ^{119}Sn) suggested that **2a** had the (*Z*)-configuration. Other phosphite ligands, such as trimethylphosphite, tri-i-propylphosphite, triphenylphosphite and trimethylolpropane phosphite (4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane), showed a comparable activity in the silastannation. The reactions using the first three phosphites were all clean, whereas the reaction using the last one, trimethylolpropane phosphite, was accompanied by the formation of small amounts of unknown products. The $Pd(OAc)_2$–$2P(OEt)_3$ combination was less effective in the present reaction. Phosphite ligands have recently been reported to be highly effective in the different reactions, the Heck reaction using aryl chlorides, by Beller and Zapf[19] and Little and Fu.[20]

The $Pd(dba)_2$–$2P(OEt)_3$-catalyzed silastannations of other arylacetylenes, prepared by the Sonogashira reaction[21–23] using aryl bromides in two steps, took place at room temperature and were completed within 5 h. The corresponding adducts **2b**–**g** with the (*Z*)-structure were obtained in 70–96% yields (Table 1). Structural proof of each adduct was also confirmed by the ^1H NMR spectra; the values of $^3J_{SnH}$ for the vinylic proton were between 147.6 and 166.0 Hz (Table 1) and are thus typical for a trans coupling.[6–8,11,24–26]

The protodemetallation of the (*Z*)-silyl(stannyl)ethenes using HCl–TEACl has not yet been reported by any groups, although the protodemetallation of the (*Z*)-1-alkyl-2-(silyl)-1-(stannyl)ethenes with HI–tetrabutylammonium iodide has been reported to give (*E*)-1-alkyl-2-silylethenes.[12] The formation of the (*E*)-silylethenes[12] has been described by the HSAB principle[15] rather than by the stabilization effect of the β-cation using silicon or stannane, i.e. a reflection of the softness of the stannyl group compared with a silyl group toward the soft iodide ion. According to this principle, in the present protodemetallation, the chloride ion as a hard base seems to favor attacking the silicon in a carbonium ion arising from the protonation of adduct **2** to form stannylethenes. However, the treatment of **2a** with HCl (20–30%) in the presence of tetraethylammonium chloride gave (*E*)-1-phenyl-2-silylethene (**3a**) with a high yield (Scheme 2). The stannylethene was not formed at all. The protodemetallations of other (*Z*)-silyl(stannyl)ethenes (**2b**–**g**) also gave only (*E*)-silylethenes (**3b**–**g**; Table 2). The experiment might clarify the fact that the $\sigma-\pi$ stabilization effect of the stannyl group in carbonium ion **4a** depicted in Scheme 3 is greater than that of the silyl group in another carbonium ion **4a′** and the conjugation effect of an aryl group. In other words, the Markownikoff-type protonation to the adduct **2** followed by attack of the chloride ion as a hard base on the silicon as a hard acid is an insignificant pathway. This also means that the carbonium ion stability dependence on the $\sigma-\pi$ stabilization effect is much more important than the HSAB principle. As a consequence, the present protodemetallation may be explained by the pathway illustrated in Scheme 3.

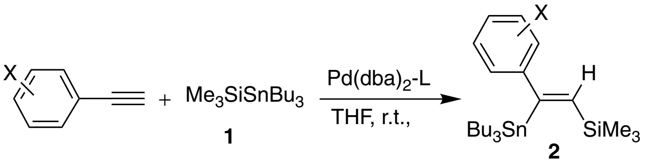
Table 1. Synthesis of (*Z*)-1-aryl-2-(silyl)-1-(stannyl)ethenes using $Pd(dba)_2$–$P(OEt)_3$ combination catalyst at room temperature[a]

Run	Ar in acetylene	Reaction time (h)	Product	Yield[b]	$^3J_{^{117}SnH}$ (H3)	$^3J_{^{119}SnH}$ (H3)
1	C_6H_5	1.5	**2a**	70	158.8	166.0
2	*p*-F C_6H_4	3	**2b**	83	158.8	164.0
3	*p*-ClC_6H_4	3	**2c**	78	155.2	162.8
4	*m*-$(CF_3)C_6H_4$	1	**2d**	90	152.8	160.0
5	*p*-$COOEtC_6H_4$	1	**2e**	96	158.8	166.0
6	*p*-$NO_2C_6H_4$	5	**2f**	71	147.6	154.8
7	*p*-CNC_6H_4	3	**2g**	92	149.2	156.0

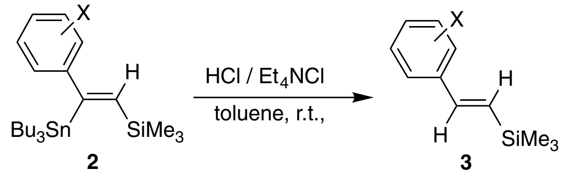
[a] A typical experiment and representative analysis are given in the Experimental section.

[b] Isolated yields by column chromatography (silica gel, hexane).

Applications of the present palladium catalyst system to other acetylenes and for the synthesis of bioactive 4-silylisoxazolines[27] using (*E*)-silylethenes are currently under way.



Scheme 1.

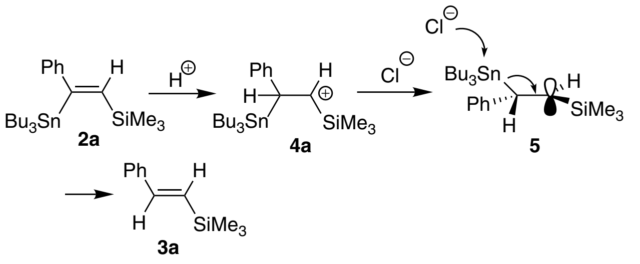


Scheme 2.

Table 2. Synthesis of (*E*)-1-aryl-2-(trimethylsilyl)ethenes by the protodestannylation of the (*Z*)-silyl(stannyl)ethenes with hydrochloric acid[a]

Run	Ar in adduct	Reaction time[b] (h)	Product	Yield[c] (%)	*J* (Hz)
1	C_6H_5	1.5	**3a**	91	19.2
2	p-FC_6H_4	3	**3b**	97	19.2
3[d]	p-ClC_6H_4	2	**3c**	99	19.2
4	m-$(CF_3)C_6H_4$	3	**3d**	98	19.0
5	p-$COOEtC_6H_4$	3	**3e**	95	19.0
6	p-$NO_2C_6H_4$	8	**3f**	93	19.2
7	p-CNC_6H_4	3	**3g**	98	19.2

[a] A typical procedure and representative analysis are given in the Experimental section.
[b] All reactions at room temperature.
[c] Isolated yields by column chromatography (silica gel, hexane).
[d] Benzene was used as the solvent.



Scheme 3.

EXPERIMENTAL

Typical procedure for silastannation of arylacetylenes

(*Z*)-1-(Tributylstannyl)-1-(*p*-chlorophenyl)-2-(trimethylsilyl) ethene (**2c**). A THF solution (1 ml) of $Pd(dba)_2$ (0.0125 g, 0.022 mmol) and triethylphosphite (0.077 g, 0.046 mmol) was stirred at room temperature under nitrogen for 5 min. To the mixture, (*p*-chlorophenyl)acetylene (0.2746 g, 2.01 mmol), the silylstannane **1** (0.3623 g, 0.997 mmol), then THF (1 ml) were added. The resulting mixture was stirred at room temperature. After 4 h, gas–liquid chromatography analysis disclosed that the silylstannane **1** was completely consumed and a new product was produced. Column chromatography (silica gel, hexane) of the mixture after removing the catalyst gave 0.34 g (78%) of analytically pure **2c**. IR (neat): 3070, 2950, 2920, 2860, 2850, 1480, 1460, 1375, 1240, 1085, 1010, 880, 860, 850, 830, 765, 690, 675 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.26 (d, 2H, $J = 8.4$ Hz), 6.90 (d, 2H, $J = 8.4$ Hz), 6.53 (s, 1H, ${}^3J_{^{119}SnH} = 162.8$ Hz, ${}^3J_{^{117}SnH} = 155.2$ Hz), 1.4 (m, 6H), 1.26 (sext. 6H, $J = 7.2$ Hz), 0.9 (m, 6H), 0.85 (t, 9H, $J = 7.2$ Hz), 0.18 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 164.8, 150.4, 149.3, 131.2, 127.9, 127.3, 29.0, 27.3, 13.6, 12, 0.1 ppm. LRMS (EI, 70 eV): 500 (M^+), 443 ($M^+ - 57$). HRMS (EI, 70 eV): calc. for $C_{23}H_{41}ClSiSn$, 500.1688; found, 500.1705.

Typical procedure for protodestannylation (*Z*)-silyl(stannyl)ethenes

(*E*)-1-(*p*-Chlorophenyl)-2-(trimethylsilyl)ethene (**3c**). To a suspension of (*Z*)-1-(tributylstannyl)-1-(*p*-chlorophenyl)-2-(trimethylsilyl)ethene (**2c**; 0.614 g, 1.228 mmol) and tetraethylammonium chloride (0.2259 g, 1.363 mmol) in benzene (4.9 ml), hydrochloric acid (20%, 1.2 ml) was added using a syringe at room temperature with stirring. After the addition was complete, the stirring was continued for 2 h. Thin-layer chromatographic of the resulting mixture disclosed that **2c** was completely consumed. Column chromatography (silica gel, hexane) gave 0.258 g (99%) of analytically pure **3c**. IR (neat): 3050, 2950, 2900, 1600, 1480, 1400, 1250, 1085, 1010, 990, 860, 840, 790, 720 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.36 (d, 1H, $J = 8.4$ Hz), 7.29 (d, 2H, $J = 8.4$ Hz), 6.81 (d, 1H, $J = 19.2$ Hz), 6.45 (d, 1H, $J = 19.2$ Hz), 0.15 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 142.2, 136.9, 133.5, 130.5, 128.7, 127.6, −1.3 ppm. LRMS (EI, 70 eV): 210 (M^+), 195 ($M^+ - 15$), 179 ($M^+ - 31$). HRMS (EI, 70 eV): calc. for $C_{11}H_{15}ClSi$, 210.0632; found, 210.0627.

REFERENCES

1. Kosugi M, Shimizu Y, Migita T. *Chem. Lett.* 1977; 301.
2. Milstein D, Stille JK. *J. Am. Chem. Soc.* 1978; **100**: 3636.
3. Stille JK. *Angew. Chem. Int. Ed. Engl.* 1986; **25**: 508.
4. Beletskaya I, Moberg C. *Chem. Rev.* 1999; **99**: 3435.
5. Suginome M, Ito Y. *Chem. Rev.* 2000; **100**: 3221.
6. Mitchell TN, Killing H, Dicke R, Wickenkamp R. *J. Chem. Soc. Chem. Commun.* 1985; 354.
7. Mitchell TN, Wickenkamp R, Amamria A, Dicke R, Schneider U. *J. Org. Chem.* 1987; **52**: 4868.
8. Chenard BL, Laganis ED, Davidson F, RajanBabu RV. *J. Org. Chem.* 1985; **50**: 3666.
9. Chenard BL, Van Zyl CM. *J. Org. Chem.* 1986; **51**: 3561.
10. Chenard BL, Van Zyl CM, Sanderson DR. *Tetrahedron Lett.* 1986; 2801.
11. Ritter K. *Synthesis* 1989; 218.
12. Mori M, Watanabe N, Kaneta N, Shibasaki M. *Chem. Lett.* 1991; 1615.
13. Mori M, Kaneta N, Shibasaki M. *J. Org. Chem.* 1991; **56**: 3486.
14. Murakami M, Amii H, Takizawa N, Ito Y. *Organometallics* 1993; **12**: 4223.
15. Ho T-l. *Hard and Soft Acids and Bases Principle in Organic Chemistry*. Academic Press; 1977.
16. Koenig KE, Weber WP. *J. Am. Chem. Soc.* 1973; **95**: 3416.
17. Utimoto K, Kitai M, Nozaki H. *Tetrahedron Lett.* 1975; 2825.
18. Lambert JB, Wang G, Teramura DH. *J. Org. Chem.* 1988; **53**: 5422.
19. Beller M, Zapf A. *Synlett* 1998; 792.
20. Littke AF, Fu GC. *Angew. Chem. Int. Ed. Engl.* 2002; **41**: 4176.
21. Sonogashira K, Tohda Y, Hagihara N. *Tetrahedron Lett.* 1975; 4467.
22. Ames DE, Bull D, Takundwa C. *Synthesis* 1981; 364.
23. Bumagin NA, Ponomaryov AB, Beletskaya IP. *Synthesis* 1984; 728.
24. Mitchell TN, Amamria A. *J. Organometal. Chem.* 1983; **252**: 47.
25. Mitchell TN, Amamria A, Killing H, Rutschow D. *J. Organometal. Chem.* 1986; **304**: 257.
26. Mitchell TN, Schneider U, Fröhling B. *J. Organometal. Chem.* 1990; **384**: C53.
27. Lukevics E, Arsenyan P, Veveris M. *Metal-Based Drugs* 1999; **5**: 251.