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Palladium Catalyzed Insertion of Norbornenes and Ethylene into Silicon–Tin σ-Bonds: Silylstannation of Alkenes with Silylstannanes

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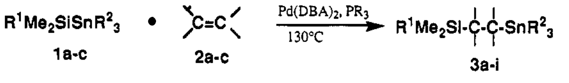
*Summary: Organosilylstannanes **1** react with norbornene (**2a**), benzonorbornadiene (**2b**), and ethylene (**2c**) at 130 °C in the presence of a catalytic amount of bis(dibenzylideneacetone)palladium combined with a trialkylphosphine to afford silylstannation products **3** in high yields.*

Activation of σ-bonds between group 14 atoms and subsequent insertions of unsaturated compounds are of current interest, since the reactions provide potent one-step transformations to afford a variety of group 14 atom compounds. Alkynes and 1,3-dienes were prevalently employed with Si–Sn,[1] Si–Si,[2] Sn–Sn,[3] and Ge–Ge[4] σ-bonds. However, as for alkenes, only a few successful reactions with ethylene or an intramolecular reaction have been reported so far. Tanaka *et al.* found that, in the presence of a catalytic amount of platinum complex, ethylene readily inserted into Si–Si σ-bonds of disilanes which have electronegative substituents on silicon atoms.[5] They also reported palladium complex catalyzed insertion of ethylene into a Ge–Ge σ-bond of 1,2-dichloro-1,1,2,2-tetramethyldigermane.[4] Ito and co-workers explored an *intramolecular* insertion of C=C bonds into Si–Si linkages of disilane moieties catalyzed by a palladium complex.[6] However, there has been no precedent for an insertion of alkenes into Si–Sn σ-bonds,[7] even though versatile silyl and stannyl functionalities are introduced simultaneously by the reaction. We disclose here the first example of insertion of alkenes into Si–Sn σ-bonds, *i.e*, silylstannation of alkene with organosilylstannanes 1 (eq 1).

Table I. Palladium Complex Catalyzed Silylstannation of Norbornenes and Ethylene[a]

entry	silylstannane	alkene	product	yield/%[b]
1	**1a**	**2a**	**3a**	89 (95)
2[c]	**1a**	**2a**	**3a**	89
3	**1b**	**2a**	**3b**	36
4	**1c**	**2a**	**3c**	94
5[d]	**1a**	**2b**[e]	**3d**	40 (42)
6	**1b**	**2b**[e]	**3e**	59
7	**1c**	**2b**[e]	**3f**	56
8	**1a**	**2c**[f]	**3g**	55 (68)
9	**1b**	**2c**[f]	**3h**	97
10	**1c**	**2c**[f]	**3i**	92

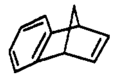
[a] Conditions: **1** (0.5 mmol), **2** (3.0 mmol), $Pd(DBA)_2$ (0.025 mmol), PBu_3 (0.10 mmol), toluene (2.0 mL) for 16 h at 130 °C. [b] Isolated yields. Numbers in parentheses show GLC yields determined by an internal standard method. [c] PEt_3 (0.050 mmol) in place of PBu_3. [d] $PdCl_2$ (0.025 mmol) in place of $Pd(DBA)_2$. [e] 1.0 mmol. [f] Initial pressure: 40 kg/cm^2.



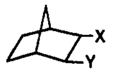
(1)

$R^1Me_2SiSnR^2_3$

1a: R^1=R^2=Me
1b: R^1=Me, R^2=Bu
1c: R^1=OMe, R^2=Bu
1d: R^1=*t*-Bu, R^2=Me
1e: R^1=*t*-Bu, R^2=Bu



2b



3a: X,Y=Me_3Si, Me_3Sn
3b: X,Y=Me_3Si, Bu_3Sn
3c: X,Y=$(MeO)Me_2Si$, Bu_3Sn

3d: X,Y=Me_3Si, Me_3Sn
3e: X,Y=Me_3Si, Bu_3Sn
3f : X,Y=$(MeO)Me_2Si$, Bu_3Sn

$R^1Me_2SiCH_2CH_2SnR^2_3$

3g: R^1=R^2=Me
3h: R^1=Me, R^2=Bu
3i : R^1=OMe, R^2=Bu

Results and Discussion

The results are listed in Table I. When (trimethylsilyl)trimethylstannane (**1a**) was allowed to react with norbornene (bicyclo[2.2.1]hept-2-ene (**2a**)) in the presence of a catalytic amount (5 mol %) of $Pd(DBA)_2$ (DBA = dibenzylideneacetone) combined with PBu_3 (P/Pd = 4.0; 20 mol %), the silylstannation product (**3a**) was obtained in excellent yield as a mixture of two enantiomers (entry 1). All the analytical data fully support the structure of

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the new compound which has exclusively exo,exo configuration. It is worth noting that norbornene gave the silylstannation product in such a high yield, while in the disilylation[5] only a low yield was achieved with norbornene as the alkene.

The nature of the catalyst precursor has a critical effect on the reaction. Naked palladium(0) complex, Pd(DBA)$_2$, combined with a basic trialkylphosphine such as PBu$_3$ (entry 1) or PEt$_3$ (entry 2) realized high catalytic activity. The effect of the catalyst system was investigated under the same reaction conditions as for entry 1. The phosphorus ligand is indispensable in the reaction, and without the addition of the ligand to Pd(DBA)$_2$ no reactions occurred. Other added phosphorus ligands to Pd(DBA)$_2$ (P/Pd = 4.0) gave less favorable results; the yield of **3a** was 11% with PMe$_3$, 0% with tricyclohexylphosphine (PCy$_3$), 7% with PPh$_3$, 7% with P(OPh)$_3$, 22% with P(OPr^i)$_3$, and 9% with P(OCH$_2$)$_3$CEt. Tetrakis(triphenylphosphine)palladium, which showed high catalytic activity in silylstannation of acetylenes with silylstannanes,[1a–f] afforded **3a** only in 12% yield. The addition of a basic[8a] trialkylphosphine with moderate steric bulk[8b] to a naked Pd(0) complex is most beneficial. However, the addition of PBu$_3$ to Pd(II) complexes (P/Pd = 4.0) also realized high catalytic activity; the yield of **3a** was 97% with PdCl$_2$ and 87% with PdCl$_2$(COD)$_2$. The tertiary phosphine might reduce the metal center to Pd(0) in situ.[9] Selected other low valent transition metal catalyst precursors (5 mol %) combined with PBu$_3$ (P/M = 4.0) showed almost no catalytic activity; the yield of **3a** was 3% with Pt(DBA)$_2$, 1% with [RhCl(COD)], and 0% with Ru(COD)(COT).

Other organosilylstannanes can be employed in the reaction. (Trimethylsilyl)tributylstannane (**1b**) also reacted with **2a** and afforded the corresponding silylstannation products selectively: exo,exo (entry 3). The methoxysilyl functionality is tolerated in the reaction, and the reaction of (methoxydimethylsilyl)tributylstannane (**1c**) with **2a** afforded **3c** exclusively in excellent yield (entry 4). In some cases,[1d,10] organosilylstannanes disproportionate to corresponding disilanes and distannanes. However, in the present reaction, such disproportionation did not occur significantly (<5%) even when yields of the silylstannation products were low.

As for the alkenes, benzonorbornadiene (**2b**) reacted with the silylstannanes (**1a**, **1b**, and **1c**) to afford the corresponding exo,exo-silylstannation products (**3d**, **3e**, and **3f**), respectively (entries 5–7). In the present reaction, all the silylstannation products (**3a–f**) with norbornene derivatives (**2a,b**) had exo,exo configurations, suggesting the silylstannanes (**1**) undergo cis additions to **2a,b** via coordination of a palladium center on a less hindered olefin face. Furthermore, in a manner similar to disilylation,[5] ethylene (**2c**) was smoothly silylstannated with **1a** to give the corresponding products (**3g**) (entry 8). Ethylene also reacted with **1b** and **1c** to afford **3h** and **3i**, respectively, in excellent yields (entries 9 and 10). However, under the standard reaction conditions 1-hexene, styrene, cyclohexene, and cyclopentene did not react with the silylstannanes at all. The steric congestion seems to affect the reaction significantly. Such a steric effect also affected the reaction of silylstannanes having bulky substituents. Thus, (*tert*-butyldimethylsilyl)trimethylstannane (**1d**) and (*tert*-butyldimethylsilyl)tributylstannane (**1e**) did not react with norbornenes (**2a,b**) nor even ethylene (**2c**) and remained intact.

In conclusion, unprecedented silylstannation of alkenes is achieved by using organosilylstannanes in the presence of a catalytic amount of a palladium complex combined with a basic trialkylphosphine.

Experimental Section

Material. The reagents and the solvents were dried and purified before use by the usual procedures.[11] Silylstannanes (**1**) were prepared by the method reported by Chenard.[1d] The following catalyst precursors and substrate were prepared by the published methods: Pd(DBA)$_2$,[12a] PdCl$_2$(COD)$_2$,[12b] Pt(DBA)$_2$,[12c] [RhCl$_2$(COD)]$_2$,[12d] Ru(COD)(COT),[12e] **2b**.[12f]

General Procedure. A typical reaction procedure is described for the synthesis of **3a**. A mixture of **2a** (282 mg, 3.0 mmol), Pd(DBA)$_2$ (14 mg, 0.025 mmol, 5 mol % based on **1a**), PBu$_3$ (20 mg, 0.10 mmol, P/Pd = 4), **1a** (119 mg, 0.50 mmol), and toluene (2.0 mL) was placed under argon flow in a 30-mL stainless steel autoclave containing an inserted glass tube. An air purge was confirmed by three pressurization (20 atm)–depressurization sequences with argon. Then the reactor was heated to 130 °C in 15 min and held at this temperature for 16 h with stirring. The reaction was terminated by rapid cooling, and the reactor was discharged. The mixture was passed through a short Florisil column (8-mm i.d. × 50 mm). GLC analysis (OV-17) with naphthalene as an internal standard showed the product (**3a**) was formed in 95% yield. The product (**3a**) was isolated by Kugelrohr distillation (Büchi) in 89% yield (pot temperature 120 °C/40 mmHg; 147 mg).

The identification of the products was made by ^{1}H- and ^{13}C-NMR and GC/MS spectra. The NMR spectra were recorded with a JEOL GX-270 spectrometer. Samples were dissolved in CDCl$_3$, and the chemical shift values were expressed relative to Me$_4$Si as an internal standard. The mass spectra were measured on Shimadzu QP-1000 (GC/MS) and Shimadzu 9020-DF (HRMS) equipped with a PAC 1100S computer system. The GLC analyses were made on a Shimadzu GC-8APF equipped with an integrater (C-R6A) with a column (3-mm i.d. × 3 m) packed with Apiezon Grease L (5% on Uniport HP, 60/80 mesh) or Silicon OV-17 (2% on Uniport HP, 60/80 mesh). Elemental analyses were performed at the Microanalytical Center of Kyoto University. The analytical data for the products are as follows.

3a: colorless liquid; ^{13}C-NMR (CDCl$_3$) δ −7.23 (q, $^1J_{Sn-C}$ = 278, 291 Hz), −1.06 (q, $^1J_{Si-C}$ = 50 Hz), 33.40 (t), 34.86 (t), 35.22 (d, $^1J_{Sn-C}$ = 397, 415 Hz), 36.29 (d, $^2J_{Sn-C}$ = 58 Hz), 38.43 (t), 39.45 (d), 42.13 (d); the ^{1}H resonances are ambiguously assigned by means of H–C COSY measurements based on ^{13}C resonances which are easily assigned on the basis of Sn–C satellite couplings; ^{1}H-NMR (CDCl$_3$) δ −0.01 (s, 9H), 0.08 (s, 9H, $^2J_{Sn-H}$ = 47, 48 Hz), 1.02 (d, 1H, J = 10 Hz), 1.17 (m, 2H), 1.29 (m, 2H), 1.46 (dd, 1H, J = 10, 1.8 Hz), 1.52–1.74 (m, 2H), 2.23 (m, 1H), 2.29 (m, 1 H); the coupling constants observed at δ 1.02 and 1.46 clearly indicated the product has a 2-exo,3-exo configuration; MS (EI) *m/e* 317

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(8) (a) Basicity (pK_a):[8c] PBu$_3$, 8.43; PEt$_3$, 8.69; PPh$_3$, 2.73; PCy$_3$, 9.70. (b) Cone angle:[8d] PBu$_3$, 132°; PEt$_3$, 132°; PPh$_3$, 143°; P(OPh)$_3$, 121°; PCy$_3$, 179°. (c) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. (d) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

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($M^+ - 15$, 14), 73 (100). Anal. Calcd for $C_{13}H_{28}SnSi$: C, 47.15; H, 8.52. Found: C, 47.41; H, 8.50.

3b: colorless liquid; pot temperature 140 °C/0.3 mmHg; ^{1}H-NMR δ −0.02 (s, 9H), 0.82–0.94 (m, 16H), 1.24–1.64 (m, 19H), 2.24 (m, 1H), 2.28 (m, 1H); ^{13}C-NMR δ −1.21 (q, $^{1}J_{\text{Si-C}} = 48$ Hz), 10.81 (t, $^{1}J_{\text{Sn-C}} = 271, 286$ Hz), 13.72 (q), 27.93 (t, $^{2}J_{\text{Sn-C}} = 41$ Hz), 29.42 (t, $^{3}J_{\text{Sn-C}} = 18$ Hz), 33.24 (d), 33.61 (t), 34.53 (t), 36.47 (d, $^{1}J_{\text{Sn-C}} = 292, 325$ Hz), 38.52 (t), 39.62 (d), 42.19 (d); MS (EI) *m/e* 458 (M^+, 0.8), 401 (21), 291 (64), 73 (100); HRMS (EI) calcd for $C_{22}H_{46}SiSn$ 458.2391, found 458.2388.

3c: colorless liquid; pot temperature 150 °C/0.3 mmHg; ^{1}H-NMR δ 0.06 (s, 3H), 0.11 (s, 3H), 0.70–0.94 (m, 17H), 1.27–1.40 (m, 12H), 1.41–1.55 (m, 6H), 2.26 (m, 1H), 2.32 (m, 1H), 3.36 (s, 3H); ^{13}C-NMR δ −3.17 (q, $^{1}J_{\text{Si-C}} = 51$ Hz), −1.90 (q, $^{1}J_{\text{Si-C}} = 52$ Hz), 10.65 (t, $^{1}J_{\text{Sn-C}} = 260, 271$ Hz), 13.77 (q), 27.82 (t, $^{2}J_{\text{Sn-C}} = 56$ Hz), 29.53 (t, $^{3}J_{\text{Sn-C}} = 20$ Hz), 30.72 (t), 31.37 (d, $^{1}J_{\text{Sn-C}} = 354, 367$ Hz), 34.00 (t, $^{2}J_{\text{Sn-C}} = 61$ Hz), 35.43 (d, $^{2}J_{\text{Sn-C}} = 70$ Hz), 38.47 (t), 39.10 (d), 41.73 (d), 49.73 (q); MS (EI) *m/e* 474 (m^+, 0.1), 415 (100), 291 (4), 89 (100); HRMS (EI) calcd for $C_{22}H_{46}OSiSn$ 474.2340, found 474.2333. Anal. Calcd for $C_{22}H_{46}OSiSn$: C, 55.82; H. 9.78. Found: C, 55.53; H, 9.80.

3d: colorless liquid; pot temperature 100 °C/0.3 mmHg; ^{1}H-NMR δ 0.33 (s, 9H), 0.42 (s, 9H, $^{2}J_{\text{Sn-H}} = 49, 51$ Hz), 1.04 (dd, 1H, $J = 1.7, 10.1$ Hz), 1.39 (dd, 1H, $J = 2.1, 10.0$ Hz), 1.64 (m, 1H), 1.85 (m, 1H), 3.56 (m, 1H), 3.64 (m, 1H), 7.26–7.45 (m, 4H); ^{13}C-NMR δ −7.33 (q, $^{1}J_{\text{Sn-C}} = 289, 301$ Hz), −0.82 (q, $J_{\text{Sn-C}} = 51$ Hz), 29.59 (d, $^{1}J_{\text{Sn-C}} = 370, 386$ Hz), 32.49 (d,$^{2}J_{\text{Sn-C}} = 55$ Hz), 46.08 (d, $^{2}J_{\text{Sn-C}} = 11$ Hz), 47.81 (t), 48.54 (d), 118.88 (d), 119.79 (d), 125.28 (d), 125.30 (d), 147.71 (s), 149.48 (s); MS *m/e* 380 (M^+, 6), 365 (95), 73 (100); HRMS (EI) calcd for $C_{17}H_{28}SiSn$ 380.0982, found 380.0989.

3e: colorless liquid; pot temperature 165 °C/0.3 mmHg; ^{1}H-NMR δ 0.15 (s, 9H), 0.93–1.04 (m, 15H), 1.22–1.69 (m, 16H), 3.41 (m, 1H), 3.56 (m, 1H), 7.08–7.20 (m, 4H); ^{13}C-NMR δ −0.82 (q, $^{1}J_{\text{Si-C}} = 50$ Hz), 10.95 (t, $^{1}J_{\text{Sn-C}} = 284, 298$ Hz), 13.74 (q), 27.68 (t, $^{2}J_{\text{Sn-C}} = 59$ Hz), 29.40 (t, $^{3}J_{\text{Sn-C}} = 21$ Hz), 30.70 (d), 32.39 (d), 46.37 (d, $^{2}J_{\text{Sn-C}} = 10$ Hz), 48.01 (t), 48.65 (d), 118.99 (d), 119.58 (d), 125.27 (d), 125.31 (d), 148.11 (s), 149.15 (s); MS (EI) *m/e* 506 (M^+, 0.1), 449 (100), 291 (37), 73 (86); HRMS (EI) calcd for $C_{26}H_{46}SiSn$ 506.2391, found 506.2405.

3f: colorless liquid; pot temperature 170 °C/0.3 mmHg; ^{1}H-NMR δ −0.15 (s, 3H), −0.05 (s, 3H), 0.60–0.67 (m, 15 H), 1.01–1.31 (m, 16H), 3.08–3.12 (m, 2 H), 3.11 (s, 3H), 6.75–6.87 (m, 4H); ^{13}C-NMR δ −2.85 (q, $^{1}J_{\text{Si-C}} = 51$ Hz), −1.48 (q, $^{1}J_{\text{Si-C}} = 57$ Hz), 10.84 (t, $^{1}J_{\text{Sn-C}} = 295, 305$ Hz), 13.74 (q), 26.60 (d, $^{1}J_{\text{Sn-C}} = 329, 344$ Hz), 27.78 (t, $^{2}J_{\text{Sn-C}} = 57$ Hz), 29.47 (t, $^{3}J_{\text{Sn-C}} = 21$ Hz), 31.15 (d), 45.91 (d, $J = 10$ Hz), 47.97 (t), 48.25 (d), 50.08 (q), 119.23 (d), 119.41 (d), 125.13 (d), 125.43 (d), 148.59 (s), 148.78 (s); MS (EI) *m/e* 522 (M^+, 0.5), 465 (100), 89 (60); HRMS (EI) calcd for $C_{26}H_{46}OSiSn$ 522.2340, found 522.2324.

3g: colorless liquid; pot temperature 75 °C/65 mmHg; ^{1}H-NMR δ −0.02 (s, 9H), 0.04 (s, 9H, $^{2}J_{\text{Sn-C}} = 49, 52$ Hz), 0.55–0.66 (m, 2H), 0.67–0.78 (m, 2H): ^{13}C-NMR δ −10.65 (q, $^{1}J_{\text{Sn-C}} = 297, 312$ Hz), −2.20 (q, $^{1}J_{\text{Si-C}} = 48$ Hz), 2.71 (t, $^{1}J_{\text{Sn-C}} = 342, 369$ Hz), 12.31 (t, $^{2}J_{\text{Sn-C}} = 48$ Hz); MS *m/e* 266 (M^+, 2), 251 (36), 73 (100); HRMS (EI) calcd for $C_{8}H_{22}SiSn$ 266.0513, found 266.0517.

3h: colorless liquid; pot temperature 80 °C/0.3 mmHg; ^{1}H-NMR δ −0.01 (s, 9H), 0.57–0.67 (m, 2H), 0.68–0.80 (m, 2H), 0.82–0.99 (m, 15H), 1.26–1.40 (m, 6H), 1.44–1.57 (m, 6H); ^{13}C-NMR δ −2.27 (q, $^{1}J_{\text{Si-C}} = 49$ Hz), 0.49 (t, $^{1}J_{\text{Sn-C}} = 299, 314$ Hz), 8.63 (t, $^{1}J_{\text{Sn-C}} = 290, 307$ Hz), 12.79 (t, $^{2}J_{\text{Sn-C}} = 49$ Hz), 13.76 (q), 27.51 (t, $^{2}J_{\text{Sn-C}} = 48$ Hz), 29.37 (t, $^{3}J_{\text{Sn-C}} = 19$ Hz); MS *m/e* 393 (M^+, 10), 291 (43), 92 (100). Anal. Calcd for $C_{17}H_{40}SiSn$: C, 52.18; H, 10.30. Found: C, 52.27; H, 10.48.

3i: colorless liquid; pot temperature 90 °C/0.3 mmHg; ^{1}H-NMR δ 0.07 (s, 6H), 0.70–0.89 (m, 19H), 1.21–1.35 (m, 6H), 1.38–1.52 (m, 6H), 3.40 (s, 3H); ^{13}C-NMR δ −3.46 (q, $^{1}J_{\text{Si-C}} = 57$ Hz), −0.45 (m, $^{1}J_{\text{Sn-C}} = 294, 307$ Hz), 8.62 (t, $^{1}J_{\text{Sn-c}} = 295, 305$ Hz), 11.71 (t, $^{2}J_{\text{Sn-C}} = 60$ Hz), 13.68 (q), 27.42 (t, $^{2}J_{\text{Sn-C}} = 49$ Hz), 29.29 (t, $^{3}J_{\text{Sn-C}} = 22$ Hz), 50.24 (q); MS *m/e* 406 (M^+, 5), 337 (52), 92 (100). Anal. Calcd for $C_{17}H_{40}OSiSn$: C, 50.13; H, 9.90. Found: C, 50.32; H, 10.01.

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