

# Supporting Information

## Remarkable Rate Acceleration of Pd(0)-Catalyzed Hydrogermylation of Alkynes and Dienes in Water

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### Instrumentation and Materials

$^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in  $\text{CDCl}_3$  as a solvent, and chemical shifts were given in  $\delta$  value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merk Silica gel 60F<sub>254</sub>. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Toluene and hexane were dried over slices of sodium. Dichloromethane was dried with molecular sieves 4A. Commercially available distilled water was used for the reaction in water. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tri(2-furyl)germane was prepared according to the reported procedure.<sup>1</sup>

### Experimental Section

**General Procedure for the Synthesis of 1-Germyl-1,3-dienes** The reaction of tri(2-furyl)germane with 1-octyne in water is representative.  $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$  (9.1 mg, 0.025 mmol), tris(2-*tert*-butylphenyl)phosphite (47.9 mg, 0.1 mmol), and 1-octyne (0.33 g, 3.0 mmol) were placed in a round-

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<sup>1</sup> Nakamura, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Synlett* **1999**, 1415

bottomed flask. Water (18 mL) was introduced and the mixture was stirred vigorously (1500 rpm) for 20 min. To the suspension was added tri(2-furyl)germane (0.27 g, 1.0 mmol) via a syringe. After stirring for 3h, the mixture was extracted with hexane (20 mL  $\times$  3). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification of the residual oil by chromatography afforded a mixture of 2-hexyl-1-[tri(2-furyl)germyl]-1,3-octadiene and 2-hexyl-3-methylene-1-[tri(2-furyl)germyl]-1-nonene (**1b** and **2b**, 94/6 regioisomeric mixture, 0.49 g, 0.99 mmol) in 99% combined yield: IR (neat) 2924, 2852, 1570, 1550, 1456, 1361, 1205, 1151, 1102, 1003, 962, 896, 813, 740 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.83–0.93 (m, 6H), 1.00–1.60 (m, 8H), 1.79 (t, *J* = 7.8 Hz, 0.12H), 1.96 (dt, *J* = 6.9, 6.6 Hz, 1.88H), 2.27 (t, *J* = 7.5 Hz, 0.12H), 2.39 (t, *J* = 7.5 Hz, 1.88H), 4.57 (s, 0.06H), 4.78 (s, 0.06H), 5.71 (s, 0.06H), 5.78 (s, 0.94H), 5.85 (dt, *J* = 15.6, 6.6 Hz, 0.94H), 6.23 (d, *J* = 15.6 Hz, 0.94H), 6.41–6.48 (m, 3H), 6.71 (d, *J* = 3.0 Hz, 0.18H), 6.76 (d, *J* = 3.0 Hz, 2.82H), 7.68 (d, *J* = 1.5 Hz, 0.18H), 7.71 (d, *J* = 1.5 Hz, 2.82H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.95, 22.44, 22.51, 26.72, 27.78, 28.66, 28.69, 28.74, 29.18, 29.25, 31.59, 31.62, 31.67, 32.66, 34.03, 35.65, 38.35, 109.80, 112.68, 115.38, 116.88, 120.75, 121.06, 131.03, 133.60, 146.91, 147.33, 150.47, 153.90, 154.55, 157.60. Found: C, 68.15; H, 7.66%. Calcd for C<sub>28</sub>H<sub>38</sub>O<sub>3</sub>Ge: C, 67.91; H, 7.73%.

**Reaction in a Separatory Funnel** Under air atmosphere, a mixture of 1-octyne (0.33 g, 3.0 mmol), the phosphite **6** (47.9 mg, 0.1 mmol), and [PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> (9.1 mg, 0.025 mmol) in water (18 mL) was placed in a separatory funnel. Tri(2-furyl)germane (0.27 g, 1.0 mmol) was added via a syringe and the whole mixture was shaken for 5 min. The mixture was extracted with hexane (20 mL  $\times$  3). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification afforded a mixture of **1b** and **2b** (94/6 regioisomeric mixture, 0.49 g, 0.99 mmol) in 99% combined yield.

**1-[Tri(2-furyl)germyl]-2,4-bis(trimethylsilyl)-1,3-butadiene (1c):** IR (neat) 2950, 2896, 1583, 1550, 1455, 1361, 1249, 1206, 1151, 1102, 1004, 984, 840, 740 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  -0.07 (s, 9H), 0.22 (s, 9H), 5.92 (d, *J* = 19.2 Hz, 1H), 6.45 (dd, *J* = 3.5, 1.8 Hz, 3H), 6.57 (s, 1H), 6.75 (dd, *J* = 3.3, 0.6 Hz, 3H), 6.86 (d, *J* = 18.5 Hz, 1H), 7.72 (d, *J* = 1.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  -1.68, -0.53, 109.82, 121.17, 134.16, 135.45, 147.33, 147.61, 153.69, 165.56. Found: C, 55.84; H, 6.45%. Calcd for C<sub>22</sub>H<sub>30</sub>O<sub>3</sub>GeSi<sub>2</sub>: C, 56.07; H, 6.42%.

**1,2,3-Trimethyl-1-[tri(2-furyl)germyl]-1,3-pentadiene (1d):** IR (neat) 3100, 2916, 2854, 1610, 1550, 1453, 1377, 1362, 1205, 1149, 1099, 1062, 1004, 896, 884, 838, 814, 741, 595  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.22 (d,  $J$  = 6.9 Hz, 3H), 1.27 (s, 3H), 1.81 (s, 3H), 1.84 (s, 3H), 5.16 (q,  $J$  = 6.75 Hz, 1H), 6.42 (dd,  $J$  = 1.5, 1.8 Hz, 3H), 6.67 (d,  $J$  = 3.0 Hz, 3H), 7.69 (d,  $J$  = 0.9 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  12.86, 14.02, 17.94, 18.43, 109.62, 120.23, 122.97, 123.31, 141.58, 146.72, 154.44, 155.40. HRMS ( $m/z$ ) Found: 384.0790. Calcd for  $\text{C}_{20}\text{H}_{22}\text{O}_3\text{Ge}$ : 140.1201.

**5-Methyl-2-(2-propenyl)-1-[tri(2-furyl)germyl]-1,3,5-hexatriene (1e):** IR (neat) 3082, 2972, 2945, 2918, 1601, 1549, 1454, 1439, 1362, 1205, 1151, 1101, 1005, 966, 897, 816, 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.61 (s, 3H), 1.99 (s, 3H), 4.97 (d,  $J$  = 21.0 Hz, 2H), 5.04 (d,  $J$  = 34.8 Hz, 2H), 6.02 (s, 1H), 6.33 (d,  $J$  = 15.8 Hz, 1H), 6.41 (d,  $J$  = 15.8 Hz, 1H), 6.46 (dd,  $J$  = 1.2, 1.8 Hz, 3H), 6.78 (d,  $J$  = 3.0 Hz, 3H), 7.73 (d,  $J$  = 1.5 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.21, 22.88, 109.82, 115.18, 118.16, 119.85, 121.15, 128.41, 136.76, 142.09, 145.51, 147.32, 153.26, 159.73. HRMS ( $m/z$ ) Found: 408.0764. Calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_3^{74}\text{Ge}$ : 408.0781.

**4-Hydroxymethyl-5-[tri(2-furyl)germyl]-2,4-pentadiene-1-ol (1f):** IR (nujol) 2954, 2900, 2864, 1589, 1550, 1478, 1456, 1392, 1361, 1261, 1234, 1205, 1150, 1101, 1063, 1003, 973, 896, 884, 814, 797, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.69 (s, 9H), 1.14 (s, 9H), 5.53 (d,  $J$  = 15.9 Hz, 1H), 5.76 (s, 1H), 5.85 (d,  $J$  = 16.2 Hz, 1H), 6.42 (dd,  $J$  = 3.2, 1.8 Hz, 3H), 6.69 (dd,  $J$  = 3.2, 0.3 Hz, 3H), 7.68 (dd,  $J$  = 1.7, 0.9 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.88, 29.46, 32.98, 38.24, 109.72, 110.95, 120.58, 125.18, 145.25, 146.75, 154.97, 170.58. Found: C, 65.40; H, 6.91%. Calcd for  $\text{C}_{24}\text{H}_{30}\text{O}_3\text{Ge}$ : C, 65.65; H, 6.89%.

**(E)-3,3-Dimethyl-1-[tri(2-furyl)germyl]-1-butene (3g):** IR (neat) 2961, 2905, 2868, 1611, 1551, 1456, 1362, 1205, 1151, 1101, 1003, 897, 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.06 (s, 9H), 5.93 (d,  $J$  = 18.3 Hz, 1H), 6.34 (d,  $J$  = 18.3 Hz, 1H), 6.46 (m, 3H), 6.76 (d,  $J$  = 3.3 Hz, 3H), 7.74 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.84, 35.80, 109.72, 113.61, 121.17, 147.42, 153.14, 161.86. HRMS ( $m/z$ ) Found: 358.0608. Calcd for  $\text{C}_{18}\text{H}_{20}\text{O}_3^{74}\text{Ge}$ : 358.0624.

**(Z)-2-Methyl-1-[tri(2-furyl)germyl]-2-butene (9):** IR (neat) 3148, 3115, 3084, 2968, 2914, 2860,

1549, 1454, 1377, 1362, 1339, 1205, 1150, 1101, 1063, 1005, 897, 885, 743  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.37 (d,  $J = 6.9$  Hz, 3H), 1.56 (s, 3H), 2.43 (s, 2H), 5.14 (q,  $J = 6.6$  Hz, 1H), 6.46 (dd,  $J = 1.8, 1.5$  Hz, 3H), 6.78 (d,  $J = 3.0$  Hz, 3H), 7.73 (d,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.31, 20.02, 25.08, 109.81, 118.97, 121.08, 131.15, 147.25, 153.03. Found: C, 59.83; H, 5.14%. Calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Ge}$ : C, 59.54; H, 5.29%.