Supporting Information

Intramolecular Aryl Migration from Tin to Carbon via a Radical Atom-Transfer Process

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Instrumentation and Materials

^{1}H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts were given in δ 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 $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Dichloromethane was dried with molecular sieves 4A. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Benzene was dried over slices of sodium. Grignard reagents were prepared from the corresponding aryl halides and Mg turning (Nacalai tesque, INC). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Experimental Section

Preparation of Aryl-(3-butenyl)dimethyltin

Phenyl magnesium bromide (1.0 M THF solution 110 mL, 110 mmol) was added to a solution of dichlorodimethyltin (11.0 g, 50 mmol) in THF (50 mL) at 0 ˚C under argon atmosphere. After stirring for 1 h at 0 ˚C, the reaction mixture was poured into 1 M NH_4Cl solution and was extracted with ethyl acetate. The organic layers were washed with brine, dried and concentrated in vacuo to give almost pure dimethyldiphenyltin (15.1 g, 50 mmol) containing a small amount of biphenyl in quantitative yield. The product was used for the next reaction without further purification.

Under argon atmosphere, trifluoroacetic acid (3.85 mL, 50 mmol) was added to the solution of dimethyldiphenyltin (15.1 g, 50 mmol) in 50 mL of THF at 0 ˚C. The resulting mixture was heated at 50 ˚C with stirring for 4 h. Evaporation of the solvent in vacuo afforded phenyldimethyltin trifluoroacetate as crystalline solid. Quantitative formation of phenyldimethyltin trifluoroacetate was checked by ^{1}H NMR. The crystal was dissolved in THF (70 mL) and 3-butenylmagnesium bromide (1 M ether solution, 60 mL, 60 mmol) was added at 0 ˚C under argon atmosphere. After stirring for 2 h, extractive workup followed by silica gel column purification provided 3-butenyldimethylphenyltin (12.6 g, 45 mmol) in 90% yield.

To synthesize functionalized aryltin compounds, further transformations were conducted as follows. Trifluoroacetic acid (0.46 mL, 6.0 mmol) was added to 3-butenyldimethylphenyltin (1.40 g, 5 mmol) in 5 mL of THF at 0 ˚C. The resulting solution was heated at 50 ˚C for 4 h with stirring. The solvent and remaining trifluoroacetic acid were distilled off under reduced pressure. The residue was dissolved with THF (5 mL) and a functionalized aryl magnesium bromide (1 M in THF, 6.0 mL, 6.0 mmol) was added at 0 ˚C. The mixture was stirred for 2 h. Extractive workup and purification by silica gel column chromatography yielded the corresponding aryl-(3-butenyl)dimethyltin (3–4 mmol). The functionalized aryl-3-butenyldimethyltin compound could also be prepared by the addition of 3-butenylmagnesium bromide to aryldimethyltin trifluoroacetate, which was obtained by the reaction of diaryldimethyltin with CF_3CO_2H. Diaryldimethyltin was easily obtained from dichlorodimethyltin with two equivalents of ArMgBr. Trifluoromethylphenylmagnesium bromide and methoxyphenylmagnesium bromide were prepared from the corresponding aryl bromide and magnesium in THF according to the usual method. *tert*-Butoxycarbonylphenylmagnesium bromide was prepared in situ by treating *tert*-butyl iodobenzoate with an equimolar amount of isopropyl magnesium bromide in THF at –40 ˚C according to the literature.[1]

Preparation of the Starting Aryl-3-iodoalkyldimethytin

The preparation of **1b** is representative. Triethylborane (1.0 mL, 1.0 M hexane solution, 1.0 mmol) was added to a solution of 3-butenyldimethylphenyltin (2.81 g, 10 mmol) and perfluorobutyl iodide (n-C_4F_9I, 3.4 mL, 20 mmol) in benzene (10 mL) at 25 ˚C under air. A slightly exothermic

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[1] Boymond, L.; Rottlä nder, M.; Cahiez, G.; Knochel, P. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1701.

reaction started immediately. After the reaction mixture was stirred for 5 h, the solvent was evaporated. Purification of the residue by silica gel column chromatography provided **1b** (4.39 g, 7.0 mmol) in 70% yield.

A Typical Procedure for Aryl Migration from Tin to Carbon

The transformation of **1b** to **3b** is representative. Triethylborane (1.0 M hexane solution, 0.1 mL, 0.1 mmol) was added to a solution of the substrate **1b** (0.63 g, 1.0 mmol) in refluxing benzene (30 mL) under air. The resulting mixture was stirred for 2 h under reflux and was concentrated in vacuo. The crude product was dissolved in THF (2 mL) under an argon atmosphere and methylmagnesium iodide (1.0 M THF solution, 1.2 mL, 1.2 mmol) was added at 0 ˚C. After stirring for 30 min at room temperature, the reaction mixture was poured into water and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The product was purified through a silica gel column to give **3b** (0.36 g, 0.70 mmol) in 70% yield.

(3-Iodo-5,5,6,6,7,7,8,8,8-nonafluorooctyl)dimethylphenyltin (1b): IR (neat) 2921, 1429, 1352, 1297, 1238, 1134, 879, 726, 699 cm-1. ^{1}H NMR ($CDCl_3$) δ 0.33 (t, *J* = 27.0 Hz, 6H), 1.00-1.23 (m, 2H), 1.90-2.12 (m, 2H), 2.74-3.00 (m, 2H), 4.32 (m, 1H), 7.37–7.58 (m, 5H). ^{13}C NMR ($CDCl_3$) δ –11.15 (t, *J* = 168 Hz), –11.12 (t, *J* = 168 Hz), 10.03 (t, *J* = 168 Hz), 25.63 (t, *J* = 39.8 Hz), 37.72, 40.38 (t, *J* = 20.8 Hz), 128.36 (t, *J* = 22.2 Hz), 128.62, 136.08 (t, *J* = 17.4 Hz), 140.68 (t, *J* = 232 Hz). ^{13}C signals of the perfluorobutyl group were not observed. Anal. Calcd for $C_{16}H_{18}F_9ISn$: C, 30.65; H, 2.89. Found: C, 30.49; H, 2.93.

(3-Phenyl-5,5,6,6,7,7,8,8,8-nonafluorooctyl)trimethyltin (3b): IR (neat) 2914, 1355, 1296, 1133, 881, 759, 715 cm-1. ^{1}H NMR ($CDCl_3$) δ 0.03 (t, *J* = 27.0 Hz, 9H), 0.51-0.70 (m, 2H), 1.72-1.96 (m, 2H), 2.30-2.48 (m, 2H), 2.95 (m, 1H), 7.15–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$) δ –10.74 (t, *J* = 162 Hz), 7.95 (t, *J* = 173 Hz), 34.21, 36.45 (t, *J* = 21.0 Hz), 42.12 (t, *J* = 29.6 Hz), 126.77, 127.62, 128.71, 143.88. Anal. Calcd for $C_{17}H_{21}F_9Sn$: C, 39.64; H, 4.11. Found: C, 39.81; H, 4.14.

(3-Iodo-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyl)(2-

methoxyphenyl)dimethyltin (8a): IR (neat) 2908, 1577, 1460, 1431, 1236, 1147 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.28 (t, *J* = 27.0 Hz, 6H), 0.98-1.20 (m, 2H), 1.90-2.07 (m, 2H), 2.76-2.93 (m, 2H), 3.79 (s, 3H), 4.33 (m, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 7.00 (t, *J* = 7.0 Hz, 1H), 7.31-7.37 (m,1H); ^{13}C NMR (CDCl$_3$) δ -10.65 (t, *J* = 172 Hz, 2C), 10.59 (t, *J* = 175 Hz), 26.32 (t, *J* = 41.5 Hz), 37.94, 40.42 (t, *J* = 20.5 Hz), 55.16, 109.20 (t, *J* = 11.4 Hz), 121.22 (t, *J* = 22.8 Hz), 129.00, 130.42, 136.61 (t, *J* = 12.8 Hz), 163.80; Anal. Calcd for $C_{21}H_{20}F_{17}IOSn$: C, 29.43; H, 2.35. Found: C, 29.72; H, 2.38.

(3-Iodo-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyl)(3-methoxyphenyl)dimethyltin (8b): IR (neat) 2908, 1585, 1476, 1411, 1210, 1042 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.32 (t, *J* = 26.5 Hz, 6H), 1.01-1.19 (m, 2H), 1.93-2.07 (m, 2H), 2.76-2.95 (m, 2H), 3.82 (s, 3H), 4.32 (m, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 7.01 (s, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 7.30 (dd, *J* = 7.5 Hz, 7.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ -10.90 (t, *J* = 170 Hz), -10.87 (t, *J* = 170 Hz), 10.09 (t, *J* = 169 Hz), 25.87 (t, *J* = 40.4 Hz), 37.67, 40.40 (t, *J* = 20.5 Hz), 55.01, 113.74, 121.57 (t, *J* = 20.0 Hz), 128.21 (t, *J* = 15.0 Hz), 129.25 (t, *J* = 25.7 Hz), 142.19 (t, *J* = 227 Hz), 159.33 (t, *J* = 27.8 Hz); Anal. Calcd for $C_{21}H_{20}F_{17}IOSn$: C, 29.43; H, 2.35. Found: C, 29.55; H, 2.33.

(3-Iodo-5,5,6,6,7,7,8,8,8-nonafluorooctyl)(2-trifluoromethylphenyl)dimethyltin (8d): IR (neat) 2916, 1438, 1237, 1122, 1031, 880, 771 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.38 (t, *J* = 27.0 Hz, 6H), 1.06-1.15 (m, 2H), 1.85-2.04 (m, 2H), 2.74-2.93 (m, 2H), 4.31 (m, 1H), 7.42-7.52 (m, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ -9.22 (t, *J* = 171 Hz), -9.15 (t, *J* = 171 Hz), 11.30 (t, *J* = 172 Hz), 25.48 (t, *J* = 40.1 Hz), 37,48, 40.35 (t, *J* = 20.5 Hz), 125.18 (q, *J* = 272.0 Hz), 126.04 (q, *J* = 4.6 Hz), 128.75, 130.98 (t, *J* = 19.5 Hz), 136.39 (t, *J* = 30.2 Hz), 137.15 (t, *J* = 13.1 Hz), 139.08; Anal. Calcd for $C_{21}H_{20}F_{17}IOSn$: C, 29.38; H, 2.47. Found: C, 29.65; H, 2.41.

(3-Iodo-5,5,6,6,7,7,8,8,8-nonafluorooctyl)(4-trifluoromethylphenyl)dimethyltin (8f): IR (neat) 1602, 1327, 1236, 1132, 1051, 879, 821, 738 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.37 (t, *J* = 26.7 Hz, 6H), 1.04-1.26 (m, 2H), 1.90-2.06 (m, 2H), 2.69-3.00 (m, 2H), 4.31 (m, 1H), 7.50-7.66 (m, 4H); ^{13}C NMR (CDCl$_3$) δ -10.97 (t, *J* = 171 Hz), -10.93 (t, *J* = 171 Hz), 10.13 (t, *J* = 172 Hz), 25.55 (t, *J* = 40.1 Hz), 37.47, 40.41 (t, *J* = 20.5 Hz), 124.40 (q, *J* = 271 Hz), 124.59 (tq, *J* = 22.2 Hz, 3.5 Hz), 130.81 (q, *J* = 32.5 Hz), 136.30 (t, *J* = 17.7 Hz), 146.34; Anal. Calcd for $C_{21}H_{20}F_{17}IOSn$: C, 29.38; H, 2.47. Found: C, 29.78; H, 2.36.

(3-Iodo-5,5,6,6,7,7,8,8,8-nonafluorooctyl)(3-*tert*-butoxycarbonylphenyl)dimethyltin (8h): IR (neat) 2974, 1713, 1294, 1237, 1134, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.36 (t, *J* = 26.7 Hz, 6H), 1.03-1.25 (m, 2H), 1.60 (s, 9H), 1.92-2.07 (m, 2H), 2.76-2.94 (m, 2H), 4.31 (m, 1H), 7.40 (dd, *J* = 7.2 Hz, 6.6 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 6.6 Hz, 1H), 8.10 (s,1H); ^{13}C NMR ($CDCl_3$) δ -10.84 (t, *J* = 172 Hz), -10.81 (t, *J* = 172 Hz), 10.14 (t, *J* = 171 Hz), 25.62 (t, *J* = 41.0 Hz), 28.07, 37.57, 40.31 (t, *J* = 20.5 Hz), 81.00, 127.96 (t, *J* = 22.5 Hz), 129.61, 131.51 (t, *J* = 20.5 Hz), 136.76 (t, *J* = 18.8 Hz), 140.02 (t, *J* = 17.7 Hz), 140.95, 166.22; HRMS (*m*/*z*): calcd for $C_{20}H_{23}F_{9}IO_{2}{}^{120}Sn$ (M^{+}-Me), 712.9583; found, 712.9625.

(3-Iodo-5,5,6,6,7,7,8,8,8-nonafluorooctyl)(4-*tert*-butoxycarbonylphenyl)dimethyltin (8i): IR (neat) 2972, 1711, 1589, 1294, 1237, 1135, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.35 (t, *J* = 26.7 Hz, 6H), 1.04-1.24 (m, 2H), 1.59 (s, 9H), 1.89-2.08 (m, 2H), 2.74-2.96 (m, 2H), 4.31 (m, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -10.87 (t, *J* = 172 Hz), -10.83 (t, *J* = 172 Hz), 10.12 (t, *J* = 171 Hz), 25.61 (t, *J* = 41.0 Hz), 28.08, 37.52, 40.31 (t, *J* = 20.5 Hz), 80.92, 128.67 (t, *J* = 22.2 Hz), 132.15, 135.85 (t, *J* = 17.6 Hz), 147.16, 166.10; HRMS (*m*/*z*): calcd for Calcd for $C_{20}H_{23}F_{9}IO_{2}{}^{120}Sn$ (M^{+}-Me), 712.9583; found, 712.9625.