

Supporting information for
“A Fe–Cu cooperative catalysis in isomerization of alkyl Grignard reagents”
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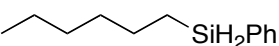
General remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM FX400 spectrometer (^1H , 400 MHz) or a JEOL JNM LA500 spectrometer (^1H , 500 MHz; ^{13}C , 125 MHz) using tetramethylsilane as an internal standard. GC spectra were taken on Shimadzu GC18A. High-resolution mass spectra were obtained with a Bruker Daltonics microTOF-Q spectrometer (ESI) or a JEOL JMS-700 spectrometer (EI). Unless otherwise noted, reagents were commercially available and used without further purification. Tetrahydrofuran and diethyl ether were purified by passing through an alumina/catalyst column system (GlassContour Co.). Alkylmagnesium halides were prepared in THF or Et_2O by the reaction of the corresponding alkyl halides with magnesium turning.

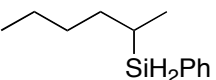
Isomerization of alkyl Grignard reagents followed by the reaction with chloro(phenyl)silane. A general procedure. A solution of FeCl_3 (1.2 mg, 0.0074 mmol for Table 1; 3.2 mg, 0.020 mmol for Scheme 7) and/or CuBr (2.2 mg, 0.015 mmol for Table 1; 5.7 mg, 0.040 mmol for Scheme 7) in addition to PBU_3 (7.5 μL , 6.1 mg, 0.030 mmol for Table 1; 20.0 μL , 16.2 mg, 0.0801 mmol for Scheme 7) in THF (2.0 mL) was placed in a 20 mL Schlenk tube and stirred for 5 min at $-25\text{ }^\circ\text{C}$. To this solution was added a THF or Et_2O solution (0.18–0.80 M) of an alkylmagnesium halide (0.30 mmol for Table 1; 0.40 mmol for Scheme 7), and the mixture was stirred at the temperature specified in Table 1 or Scheme 7. After the time specified in Table 1 or Scheme 7, chloro(phenyl)silane (80 μL , 86 mg, 0.60 mmol for Table 1; 107 μL , 114 mg, 0.800 mmol for Scheme 7) was added, and stirred at $30\text{ }^\circ\text{C}$ (Table 1) or $60\text{ }^\circ\text{C}$ (Scheme 7) for 2 h. To this solution were added water (1 mL) and nonane (internal standard for GC analysis), and the resulting mixture was diluted with diethyl ether (2 mL). An aliquot of the organic layer was subjected to GC analysis. The yields and the isomer ratios were determined by GC using nonane as an internal standard. As for entry 1 of Table 1 and Scheme 7, the alkylsilanes were isolated as follows. After extraction with diethyl ether (5 mL x 3) from the reaction mixture above, the combined organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification with PTLC (SiO_2 : hexane) gave 1-hexyl(phenyl)silane (**4**: 47 mg, 81%) or phenyl(1-phenylethyl)silane (**23**: 59 mg, 69%).

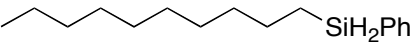
A representative procedure for preparation of the authentic samples of alkyl(phenyl)silanes: 3-hexyl(phenyl)silane (15). To an Et_2O solution (0.37 M) of 3-hexylmagnesium bromide (**14**: 1.35 mL, 0.50 mmol) in THF (3.0 mL) was added chloro(phenyl)silane (133 μL , 142 mg, 1.00 mmol), and the mixture was stirred at $30\text{ }^\circ\text{C}$ for 2 h. To this solution was added water (1 mL), and the resulting mixture was extracted with diethyl ether (4 mL x 2). The combined organic layer was washed with brine (5 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification with PTLC (SiO_2 : hexane) gave 3-hexyl(phenyl)silane (**15**: 87 mg, 91%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, $J = 7.2$ Hz, 3 H), 0.95 (t, $J = 7.5$ Hz, 3 H), 1.02–1.09 (m, 1 H), 1.34–1.41 (m, 2 H), 1.43 (quint, $J = 6.9$ Hz, 2 H), 1.47–1.56 (m, 2 H), 4.25 (d, $J = 2.9$ Hz, $^1J_{\text{Si-H}} = 191$ Hz, 2 H), 7.32–7.41 (m, 3 H), 7.55–7.59 (m, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ 13.2, 14.3, 21.8, 23.9, 24.1, 33.1, 127.9, 129.4, 132.6, 135.6. HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{20}\text{Si}$: M^+ , 192.1334. Found: m/z 192.1330.

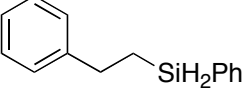
Other alkylsilanes **4**, **3**, **16**, phenyl(2-phenylethyl)silane and **23** have already been reported in the

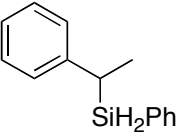
literature. Their ^1H NMR data are as follows.

 **1-Hexyl(phenyl)silane (4).**^[1] 94% yield (reaction temperature = 30 °C). A colorless oil. ^1H NMR (500 MHz, C_6D_6) δ 0.79–0.84 (m, 2 H), 0.86 (t, $J = 7.2$ Hz, 3 H), 1.12–1.30 (m, 6 H), 1.34–1.44 (m, 2 H), 4.51 (t, $J = 3.7$ Hz, $^1J_{^{29}\text{Si-H}} = 191$ Hz, 2 H), 7.13–7.19 (m, 3 H), 7.49–7.55 (m, 2 H). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, $J = 7.0$ Hz, 3 H), 0.91–0.97 (m, 2 H), 1.21–1.32 (m, 4 H), 1.35 (quint, $J = 6.9$ Hz, 2 H), 1.41–1.49 (m, 2 H), 4.28 (t, $J = 3.7$ Hz, $^1J_{^{29}\text{Si-H}} = 192$ Hz, 2 H), 7.32–7.42 (m, 3 H), 7.54–7.59 (m, 2 H).

 **2-Hexyl(phenyl)silane (3).**^[1] 94% yield (reaction temperature = 30 °C). A colorless oil. ^1H NMR (500 MHz, C_6D_6) δ 0.84 (t, $J = 7.2$ Hz, 3 H), 1.02–1.07 (m, 4 H), 1.12–1.41 (m, 5 H), 1.46–1.56 (m, 1 H), 4.42–4.45 (m, 1 H), 4.46–4.49 (m, 1 H), 7.12–7.18 (m, 3 H), 7.51–7.56 (m, 2 H). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, $J = 7.2$ Hz, 3 H), 1.06 (d, $J = 7.1$ Hz, 3 H), 1.09–1.20 (m, 1 H), 1.21–1.56 (m, 6 H), 4.19 (dd, $J = 6.0, 3.3$ Hz, $^1J_{^{29}\text{Si-H}} = 191$ Hz, 1 H), 4.23 (dd, $J = 6.0, 2.6$ Hz, $^1J_{^{29}\text{Si-H}} = 191$ Hz, 1 H), 7.32–7.42 (m, 3 H), 7.54–7.59 (m, 2 H).

 **1-Decyl(phenyl)silane (16).**^[2] 98% yield (reaction temperature = 30 °C). A colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 7.0$ Hz, 3 H), 0.90–0.97 (m, 2 H), 1.20–1.38 (m, 14 H), 1.41–1.49 (m, 2 H), 4.28 (t, $J = 3.7$ Hz, $^1J_{^{29}\text{Si-H}} = 192$ Hz, 2 H), 7.32–7.42 (m, 3 H), 7.54–7.59 (m, 2 H).

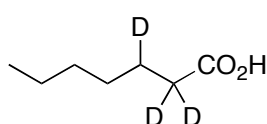
 **Phenyl(2-phenylethyl)silane.**^[1] 97% yield (reaction temperature = 60 °C). A colorless oil. ^1H NMR (500 MHz, C_6D_6) δ 1.10 (tt, $J = 8.4, 3.6$ Hz, 2 H), 2.61 (t, $J = 8.4$ Hz, 2 H), 4.45 (t, $J = 3.6$ Hz, $^1J_{^{29}\text{Si-H}} = 193$ Hz, 2 H), 7.00 (d, $J = 7.6$ Hz, 2 H), 7.06 (t, $J = 7.4$ Hz, 1 H), 7.12–7.19 (m, 5 H), 7.42–7.47 (m, 2 H). ^1H NMR (500 MHz, CDCl_3) δ 1.30 (tt, $J = 8.4, 3.7$ Hz, 2 H), 2.77 (t, $J = 8.4$ Hz, 2 H), 4.32 (t, $J = 3.7$ Hz, $^1J_{^{29}\text{Si-H}} = 194$ Hz, 2 H), 7.13–7.23 (m, 3 H), 7.27 (t, $J = 7.6$ Hz, 2 H), 7.32–7.44 (m, 3 H), 7.56 (d, $J = 7.7$ Hz, 2 H).

 **Phenyl(1-phenylethyl)silane (23).**^[1] 92% yield (reaction temperature = 60 °C). A colorless oil. ^1H NMR (500 MHz, C_6D_6) δ 1.33 (d, $J = 7.6$ Hz, 3 H), 2.41 (qt, $J = 7.6, 3.3$ Hz, 1 H), 4.47 (dd, $J = 6.8, 3.3$ Hz, $^1J_{^{29}\text{Si-H}} = 196$ Hz, 1 H), 4.49 (dd, $J = 6.8, 3.3$ Hz, $^1J_{^{29}\text{Si-H}} = 196$ Hz, 1 H), 6.98–7.04 (m, 3 H), 7.05–7.16 (m, 5 H), 7.30–7.36 (m, 2 H). ^1H NMR (500 MHz, CDCl_3) δ 1.45 (d, $J = 7.5$ Hz, 3 H), 2.62 (qt, $J = 7.5, 3.4$ Hz, 1 H), 4.31 (dd, $J = 6.8, 3.4$ Hz, $^1J_{^{29}\text{Si-H}} = 197$ Hz, 1 H), 4.33 (dd, $J = 6.8, 3.4$ Hz, $^1J_{^{29}\text{Si-H}} = 197$ Hz, 1 H), 7.06–7.14 (m, 3 H), 7.24 (t, $J = 7.7$ Hz, 2 H), 7.30 (t, $J = 7.6$ Hz, 2 H), 7.35–7.42 (m, 3 H).

Iron-copper-catalyzed isomerization of 2-hexylmagnesium bromide followed by reaction with benzaldehyde (Scheme 1). A solution of FeCl_3 (2.8 mg, 18 μmol), CuBr (5.0 mg, 35 μmol) and PBU_3 (17 μL , 14 mg, 70 μmol) in THF (2.0 mL) was placed in a 20 mL Schlenk tube and stirred for 5 min at -25 °C. To this solution was added an Et_2O solution (0.58 M) of 2-hexylmagnesium bromide (**1a**: 1.2 mL, 0.70 mmol), and the mixture was stirred for 10 min at -25 °C. Benzaldehyde (50 mg, 0.47 mmol) was added at -25 °C, and the stirring was continued for another 10 min. After a 10% NH_4Cl aqueous solution (10 mL) was added, the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification with PTLC (SiO_2 : hexane/ethyl acetate = 4/1) gave 1-phenyl-1-

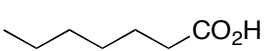
heptanol^[3] (**5**: 75 mg, 83%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, *J* = 6.9 Hz, 3 H), 1.20–1.35 (m, 7 H), 1.36–1.46 (m, 1 H), 1.65–1.74 (m, 1 H), 1.75–1.85 (m, 1 H), 1.84 (d, *J* = 3.2 Hz, 1 H), 4.66 (td, *J* = 6.7, 3.2 Hz, 1 H), 7.24–7.30 (m, 1 H), 7.32–7.37 (m, 4 H).

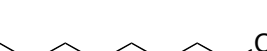
Iron–copper-catalyzed isomerization of alkyl Grignard reagents followed by reaction with CO₂ (Schemes 1 and 2): A general procedure. A solution of FeCl₃ (2.4 mg, 15 μmol), CuBr (4.3 mg, 30 μmol) and PBu₃ (15 μL, 12 mg, 60 μmol) in THF (2.0 mL) was placed in a 20 mL Schlenk tube and stirred for 5 min at –25 °C. To this solution was added an Et₂O solution (0.24–0.84 M) of an alkylmagnesium halide (0.30 mmol), and the mixture was stirred at –25 °C for 10 min. After CO₂ gas (dried by passing through conc. H₂SO₄) was bubbled for 1 h at –10 °C, a 1 M HCl aqueous solution (3 mL) was added, and the resulting mixture was extracted with ethyl acetate (5 mL x 3). After evaporation of the solvent, the residue was diluted with diethyl ether (5 mL), and acidic compounds were extracted with a 1 M NaOH aqueous solution (5 mL x 2). The combined aqueous layer was acidified with a 1 M HCl aqueous solution (15 mL) and extracted with ethyl acetate (20 mL x 2). The combined organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the corresponding linear carboxylic acid. ¹H NMR showed that no branch isomers were included.

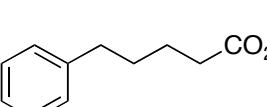


2,2,3-Trideuterioheptanoic acid (6a-d₃). A colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, *J* = 6.8 Hz, 3 H), 1.21–1.40 (m, 6 H), 1.55–1.70 (m, 1.02 H), 2.28–2.42 (m, 0.27 H). ¹H NMR is consistent with the corresponding non-deuterated carboxylic acid (**6a**). HRMS shows that it contains a mixture of di-, tri- and tetradeuterated heptanoic acids. HRMS (ESI) Calcd for C₇H₁₁D₃O₂: [M–H][–], 131.104657. Found: *m/z* 131.104694; Calcd for C₇H₁₀D₃O₂: [M–H][–], 132.110933. Found: *m/z* 132.111408; Calcd for C₇H₉D₄O₂: [M–H][–], 133.117210. Found: *m/z* 133.116608.

Carboxylic acids **6a**, **6b** and **6c** have already been reported in the literature. Their ¹H NMR data are as follows.

 **Heptanoic acid (6a).** A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 0.89 (t, *J* = 6.9 Hz, 3 H), 1.22–1.40 (m, 6 H), 1.64 (quint, *J* = 7.5 Hz, 2 H), 2.35 (t, *J* = 7.5 Hz, 2 H).

 **Nonanoic acid (6b).** A colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, *J* = 6.8 Hz, 3 H), 1.18–1.41 (m, 10 H), 1.63 (quint, *J* = 7.6 Hz, 2 H), 2.35 (t, *J* = 7.6 Hz, 2 H).

 **5-Phenylpentanoic acid (6c).** A white crystal. ¹H NMR (500 MHz, CDCl₃) δ 1.64–1.73 (m, 4 H), 2.38 (t, *J* = 7.2 Hz, 2 H), 2.64 (t, *J* = 7.1 Hz, 2 H), 7.18 (d, *J* = 8.1 Hz, 2 H), 7.15–7.21 (m, 1 H), 7.27 (t, *J* = 8.0 Hz, 2 H).

Isomerization of 2-octylmagnesium chloride in the presence of a stoichiometric amount of FeCl₃ or CuBr (Scheme 3). To a solution of FeCl₃ (10 mg, 0.062 mmol) or CuBr (8.9 mg, 0.062 mmol) in addition to PBu₃ (50 mg, 0.25 mmol for FeCl₃; 25 mg, 0.13 mmol for CuBr) in THF (2.0 mL) was placed in a 20 mL Schlenk tube and stirred for 5 min at –25 °C. To this solution was added an Et₂O solution (0.65 M) of 2-octylmagnesium chloride (**1b**: 0.57 mL, 0.37 mmol), and the mixture was stirred for 10 min at –25 °C. After D₂O (0.70 mL), Cl₂CDCDCl₂ (internal standard for ²H NMR analysis) and Et₂O (1.0 mL)

were added, an aliquot (0.2 mL) of the organic layer was diluted with CHCl₃ (0.5 mL) and subjected to ²H NMR analysis. The yield of 1-deuteriooctane (**7**) was determined using Cl₂CDCDCl₂ as an internal standard.

Iron–copper-catalyzed reaction of 3-hexylmagnesium bromide in the absence or presence of 1-decene (Scheme 5). A solution of FeCl₃ (2.4 mg, 0.015 mmol), CuBr (4.3 mg, 0.030 mmol) and PBu₃ (15 μL, 12 mg, 0.060 mmol) with or without 1-decene (42 mg, 0.30 mmol) in THF (2.0 mL) was placed in a 20 mL Schlenk tube and stirred for 5 min at –25 °C. To this solution was added an Et₂O solution (0.45 M) of 3-hexylmagnesium bromide (**14**: 0.67 mL, 0.30 mmol), and the mixture was stirred at –25 °C. After 10 min, chloro(phenyl)silane (80 μL, 0.60 mmol) was added and stirred for 2 h at 30 °C. To this solution were added water (1 mL) and nonane (internal standard for GC analysis), and the resulting mixture was diluted with diethyl ether (2 mL). An aliquot of the organic layer was subjected to GC analysis. The yields and the isomer ratios were determined by GC using nonane as an internal standard.

References

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