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REVISED

Supplemental Material for

Cross-Coupling Reactions of Aryl Chlorides with Organochlorosilanes: Highly Effective Methods for Arylation or Alkenylation of Aryl Chlorides

Ken-ichi Gouda, Emiko Hagiwara, Yasuo Hatanaka,*,† and Tamejiro Hiyama‡

Sagami Chemical Research Center

4-4-1 Nishiohnuma, Sagamihara, Kanagawa, 229, Japan

‡Research Laboratory of Resources Utilization, Tokyo Institute of Technology

4259 Nagatsuda, Midori-ku, Yokohama, 226, Japan

†Present address: Department of Organic Chemistry, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan.

EXPERIMENTAL

General. All melting points were uncorrected. The ^{1}H NMR spectra were recorded on a Brucker AC-200P (200 MHz) or a Brucker AM-400 (400 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Infrared spectra were obtained on a JASCO A-202 spectrometer. Elemental analyses were carried out on a Perkin Elmer Model 240. Mass spectra were recorded on a Hitachi M-80 (low-resolution mass spectra) or a Hitachi M-80BS (high-resolution mass spectra). *N,N*-dimethylformamide (DMF) was distilled at reduced pressure from calcium hydride. Potassium fluoride (spray dried) was purchased from Wako Chemical Co. and used without further purification. All chloroarenes used in this work are commercially available.

Organochlorosilanes. Trichloro(4-methoxyphenyl)silane was obtained from Shin-etsu Chemical Co. and used without further purification. (Chloro)(4-methoxyphenyl)(dimethyl)silanen was prepared by the literature procedures (Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886).

(Dichloro)(ethyl)(4-methoxyphenyl)silane. A solution of (4-methoxyphenyl)magnesium bromide prepared from 4-bromoanisole (5.6 g, 30 mmol) and magnesium (0.88 g, 36 mmol) in THF (15 mL) was added dropwise over 20 min to a solution of (trichloro)(ethyl)silane (4.91 g, 30 mmol) in THF (35 mL) at 0 °C . After the solution was stirred at the room temperature for 12 h, the bulk of the solvent was removed under reduced pressure and dry hexane (50 mL) was added to the reaction mixture to precipitate magnesium salt. The resulting slurry was filtered and the filtrate was concentrated under reduced pressure (1 mm for 2 h) to give (dichloro)(ethyl)(4-methoxyphenyl)silane as a brown oil which was pure enough for the use in the cross-coupling reactions without further purification (6.9 g, 29 mmol, 97%): bp 109 °C (1.7 mm); IR (neat) 3060, 2960, 1597, 1286, 1119, 821, 698 cm^{-1}; ^1H NMR (90 MHz): d 0.95-1.45 (m, 5H), 3.84 (s, 3H), 6.97 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H); HRMS for $C_9H_{12}OSiCl_2$ calcd 234.0033, found 234.0030.

(Dichloro)(ethyl)(4-methylphenyl)silane . To a solution of ethyltrichlorosilane (10.0 g, 60 mmol) in THF (50 mL) was added at 0 °C with stirring 4-methylphenylmagnesium bromide prepared from 4-bromotoluene (10.3 g, 60 mmol) and magnesium (1.94 g, 80 mmol) in ether (30 mL). After stirring at room temperature overnight, bulk of the solvent was removed under reduced pressure, and dry hexane was added to the reaction mixture to precipitate magnesium salt. The resulting slurry was filtered and the filtrate was concentrated under reduced pressure (1 mm for 2 h) to give dichloro(ethyl)(4-methylphenyl)silane as a brown oil which was pure enough for the use in the cross-coupling reactions without further purification (13.0 g,

98%): IR (neat) 2965, 2880, 1600, 1460, 1250, 1115, 1015, 800, 700 cm^{-1}; ^1H NMR (90 MHz) d 0.90-1.53 (m, 5 H), 2.42 (s, 3 H), 7.24 (d, J = 8.0 Hz, 2 H), 7.55 (d, J = 8.0 Hz, 2 H).

(*E*)-1-(Methyldichlorosilyl)-1-hexene. Hydrosilylation of 1-hexene (14.3 g, 170 mmol) with methyldichlorosilane (20 g, 18 mmol) was carried out using 0.1 mol% of H_2PtCl_6 in 2-propanol (0.2 M, 0.85 mL) at 80 °C according to the literature (Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Kumada, M. *Organometallics* **1982**, *1*, 355.), giving (*E*)-1-(methyldichlorosilyl)-1-hexene as a colorless liquid (28 g, 84%): IR (neat) 2975, 2940, 2880, 2870, 1625, 1265, 830, 800, 780 cm^{-1}; ^1H NMR (200 MHz) δ 0.83 (s, 3H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.25-1.55 (m, 4H), 2.22 (m, 2H), 5.74 (d, *J* = 18.5 Hz, 1H), 6.50 (dt, *J* = 18.5, 6.3 Hz, 1H).

(*Z*)-1-(ethyldichlorosilyl)-1-octene A solution of (Z)-octenylmagnesium bromide prepared from (Z)-1-bromo-1-octene (3.0 g, 16 mmol) and magnesium (0.48 g, 20 mmol) in THF (15 mL) was slowly added to a solution of trichloroethylsilane (3.0 g, 18 mmol) in THF (15 mL) at 0 °C. After the solution was stirred at the room temperature for 12 h, the bulk of the solvent was removed under reduced pressure and dry hexane (15 mL) was added to the reaction mixture to precipitate magnesium salt. The resulting slurry was filtered and the filtrate was concentrated under reduced pressure to give (Z)-1-(ethyldichlorosilyl)-1-octene as a colorless liquid which was pure enough for the use in the cross-coupling reactions without further purification (3.3 g, 14 mmol, 87%): IR (neat) 2975, 2930, 2870, 1615, 1020, 750, 710, 570 cm^{-1}; ^1H NMR (200 MHz): δ 0.89 (t, *J* = 6.6 Hz, 3 H), 1.09-1.50 (m, 13 H), 2.30 (q, *J* = 7.6 Hz, 2H), 5.60 (d, *J* = 13.7 Hz, 1H), 6.58 (dt, *J* = 13.7, 7.6 Hz, 1H).

General procedure for the palladium-catalyzed cross-coupling reactions of aryl(dichloro)(ethyl)silanes with chloroarenes is described in the text (ref. 10).

Following compounds were prepared according to the general procedure.

4-acetyl-4'-methoxybiphenyl (Table 1, entries 1, 2): colorless crystal; mp 77 °C, lit, 75-76 °C (Ried, W.; Schubert, H. J. *Ann.* **1962**, *653*, 181); IR (KBr) 2950, 2850, 1680, 1600, 1200, 820 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.62 (s, 3H), 3.85 (s, 3H), 6.99 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H); MS (EI) m/z (%) 226 (M^+, 75), 211 (100), 183 (12), 168(18).

3-acetyl-4'-methoxylbiphenyl (Table 1, entry 3): colorless crystal; mp 48-49 °C ; IR (KBr) 1680, 1250, 840, 800, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ2.63 (s, 3H), 3.84 (s, 3H), 6.99 (d, J = 8.7 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 8.7 Hz, 2H), 7.73 (dd, J = 7.7, 1.7 Hz, 1H), 7.88 (dd, J = 7.7, 1.7 Hz, 1H), 8.13 (t, J = 1.7 Hz, 1H); MS (EI) m/z (%) 226 (M^+, 100), 211 (64), 183 (34), 168(19), 152(11); HRMS for $C_{15}H_{14}O_2$ calcd 226.0992, found 226.0989.

3,4-difluoro-4'-methylbiphenyl (Table 1, entry 4): colorless crystal; mp 47.5-48.0 °C; IR (KBr) 2950, 1600, 1530, 1500, 1310, 1275, 1180, 1120, 1030, 1005, 810, 780 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ2.38 (s, 3H), 7.18 (dt, J = 10.2, 8.3 Hz, 1H), 7.23 (d, J = 8.2 Hz, 2H), 7.25 (m, 1H), 7.35 (ddd, J = 11.7, 7.6, 2.2 Hz, 1H), 7.40 (d, J = 8.2 Hz, 2H); Anal. Calcd for $C_{13}H_{10}F_2$: C, 76.46; H, 4.94. Found: C, 76.50; H, 4.88.

4-methyl-4'-trifluoromethylbiphenyl (Table 1, entry 5): colorless crystal; mp 120 °C, lit, 121 °C (Brune, H. A.; Reiner, H.; Schmidtberg, G. Z. *Naturforsch, B: Anorg. Chem. Org. Chem.* **1984**, *39B*, 1772); IR (KBr) 1300, 1140, 1120, 1080, 820 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ2.40 (s, 3H), 7.26 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.66 (s, 4H); MS (EI) m/z (%) 236 (M^+, 100), 167 (34).

4-cyano-4'-methoxybiphenyl (Table 1, entries 6-9): colorless crystal; mp 103-104 °C, lit, 104 °C (Gray, G. W.; Mosley, A. *J. Chem. Soc., Perkin Trans. 2,* **1976**, 97); IR (KBr) 2220, 1600, 1490. 1240, 1175, 1135, 825 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.85 (s, 3H), 7.00 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H).

Synthesis of 3,4-difluoro-4'-(*trans*-4-propylcyclohexyl)-1,1'-biphenyl (2) (Table1, entry 10).

(Dichloro)(ethyl)[4-(trans-4-propylcyclohexyl)phenyl]silane. (1)

A mixture of 8.43 g (30 mmol) of 1-bromo-4-(*trans*-4-propyl-cyclohexyl)benzene and 0.88 g (36 mmol) of magnesium in 30 mL of THF was heated to 50 °C for 3 h. This solution was added dropwise over a period of 30 min to a solution of 5.4 g (33 mmol) of trichloroethylsilane in 20 mL of THF at 0 °C. After stirring at room temperature overnight, bulk of the solvent was removed under reduced pressure, and 50 mL of dry hexane was added to the reaction mixture to precipitate magnesium salt. The resulting slurry was filtered and the filtrate was concentrated under reduced pressure (1 mm for 2 h) to give (dichloro)(ethyl)[4-(*trans*-4-propylcyclohexyl)phenyl]silane (**1**) (9.34 g, 28.3 mmol, 95%) as a viscous liquid which was pure enough for the use in the next reaction without further purification: IR (KBr) 2960, 2920, 1600. 1450, 1260, 1120, 1015, 815, 700, 570, 550, 515 cm^{-1}; ^1H NMR (200 MHz) d 0.90 (t, J = 6.9 Hz, 3H), 1.00-1.58 (m, 14H), 1.80-1.95 (m, 4H), 2.50 (t, J = 12 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H).

3,4-difluoro-4'-(trans-4-propylcyclohexyl)-1,1'-biphenyl (**2**)

To a suspension of 0.25 g (4.4 mmol) of pottasium fluoride (spray dried) in DMF (1.2 mL) was added 0.29 g (0.87 mmol) of (dichloro)(ethyl)[4-(*trans*-4-propylcyclohexyl)phenyl]silane (**1**) at 0 °C under an atmosphere of argon. The resulting reaction mixture was then stirred at 60 °C for 3 h. The reaction was

allowed to cool to room temperature, and 2.2 mg (0.05 mmol) of $(i\text{-}Pr_3P)_2PdCl_2$ and 0.14 g (1.0 mmol) of 3,4-difluorochlorobenzene was added. The resulting reaction mixture was heated at 150 °C for 20 h and then cooled to room temperature, poured into a saturated aqueous sodium chloride solution and extracted with ethyl acetate. Removal of the solvent under reduced pressure afforded a crude product which was purified by silica-gel column chromatography (hexane:ethyacetate=5:1) to give 0.165 g (0.56 mmol, 64%) of 3,4-difluoro-4'-(*trans*-4-propylcyclohexyl)-1,1'-biphenyl (**1**) as a colorless crystal: mp 105-107 °C; IR (KBr) 2970, 2940, 1610, 1510, 815, 780 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ0.91 (t, *J* = 7.0 Hz, 3H), 1.00-1.60 (m, 9H), 1.80-2.00 (m, 4H), 2.50 (tt, J = 2.1, 3.1 Hz, 1H), 7.17 (dt, J = 9.7, 8.3 Hz, 1H), 7.23-7.30 (m, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.35 (m, 1H), 7.43 (d, J = 8.2 Hz, 2H); Anal. Calcd for $C_{21}H_{24}F_2$: C, 80.22; H, 7.69. Found: C, 80.20; H, 7.73.

General Procedure for the Palladium-Catalyzed Cross-Coupling Reactions of Alkenyl(dichloro)(alkyl)silanes with Chloroarenes. (*E*)-1-(4-cyanophenyl)-1-hexene (Table 1, entry 11). To a solution of tetrabutylammonium fluoride in THF (1.0 M, 2.0 mL, 2.0 mmol) were added 69 mg (0.50 mmol) of 4-chlorobenzonitrile and 5.4 mg (0.013 mmol) of dichlorobis(triethylphosphine)palladium (II). The solution was degassed by three freeze-pump-thaw cycle. To this solution was added 118 mg (0.60 mmol) of (*E*)-1-[dichloro(methy)lsilyl]-1-hexene at 0 °C. After stirring at room temperature for 30 min, the reaction mixture was then heated at 90 °C for 20 h in a sealed tube. The solution was cooled to room temperature, poured into 5 mL of water, extracted with ethy acetate (2 X 5 mL), and then dried ($MgSO_4$). Concentration and purification of the crude material by column chromatography (silica-gel) using ethyl acetate/hexane (1:7) gave 76 mg (83%) of (*E*)-1-(4-cyanophenyl)-1-hexene as a colorless oil: IR (neat) 3050, 2970, 2940, 2240, 1715, 1655, 1610, 1510, 1470, 1420, 1390, 985, 860, 835, 820, 560 cm^{-1}; ^1H

NMR (200 MHz) δ 0.93 (t, J = 7.0 Hz, 3H), 1.27-1.54 (m, 4H), 2.18-2.30 (m, 2H), 6.34-6.40 (m, 2H), 7.40 (d, J = 8.2 Hz, 2H) 7.56 (d, J = 8.2 Hz, 2H); MS (EI) m/z (%) 185 (M^+, 26), 142 (47), 129 (100); Anal. Calcd for $C_{13}H_{15}N$: C, 84.23; H, 8.16. Found: C,84.16 ; H, 8.19.

The following compounds were prepared in an analogous fashion:

(*E*)-1-(3-acetylphenyl)-1-hexene (Table 1, entry 12): colorless oil: IR (neat) 2950, 2920, 2860, 1610, 1325, 1160, 1120, 1105, 1065, 1010, 965 cm^{-1}; ^1H NMR (200 MHz) δ 0.93 (t, J = 7.0 Hz, 3H), 1.28-1.56 (m, 4H), 2.23 (td, J = 6.8, 6.3 Hz, 2H), 2.60 (s, 3H), 6.30 (dt, J = 16.0, 6.3 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.92 (s, 1H); MS (EI) m/z (%) 202 (M^+, 11), 43 (100); Anal. Calcd for $C_{14}H_{18}O$: C, 84.12; H, 9.00. Found: C, 84.15; H, 8.92 .

(*Z*)-1-(4-cyanophenyl)-1-octene (Table 1, entry 13): colorless oil: IR (neat) 2950, 2930, 2850, 2250, 1605, 855 cm^{-1}; ^1H NMR (200 MHz) δ 0.87 (t, J = 6.5 Hz, 3H), 1.20-1.55 (m, 8H), 2.19-2.36 (m, 2H), 5.82 (td, J = 7.4, 11.5 Hz, 1H), 6.40 (d, J = 11.5 Hz, 1H), 7.35 (d, J = 8.3Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H); MS (EI) m/z (%) 213 (M^+, 13), 129 (100); Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98 Found: C, 84.27; H, 8.87.

(*Z*)-1-[4-(trifluoro)phenyl]-1-octene (Table 1, entry 14): colorless oil: IR (neat) 2950, 2930, 2850, 1615, 1330, 1165, 1130, 1070, 850 cm^{-1}; ^1H NMR (200 MHz) δ 0.87 (t, J = 6.6 Hz, 3H), 1.20-1.49 (m, 8H), 2.25-2.39 (m, 2H), 5.77 (dt, J = 11.7, 7.3 Hz, 1H), 6.41 (d, J = 11.7 Hz, 1H), 7.36 (d, J = 8.3Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H); MS (EI) m/z (%) 256 (M^+, 15), 237 (4), 185 (19), 172 (100); Anal. Calcd for $C_{15}H_{19}F_3$: C, 70.29; H, 7.47. Found: C, 70.11; H, 7.69.