Synthesis Of Unsymmetrical Biaryls Via Arylsilacyclobutanes

Scott E. Denmark,* and Zhicai Wu

Roger Adams Laboratory, Department of Chemistry, University of Illinois
Urbana, Illinois 61801

SUPPORTING INFORMATION

General Experimental

NMR data were collected on a Varian Unity-400 (400 MHz ^{1}H, 100.6 MHz ^{13}C), or a Varian Unity-500 (500 MHz ^{1}H, 125.8 MHz ^{13}C) in the University of Illinois School of Chemical Sciences Varian/Oxford Instrument Center for Excellence in NMR laboratory. ^{1}H NMR spectra were obtained in deuteriochloroform ($CDCl_3$) with either tetramethylsilane (TMS, $\delta = 0.00$ for ^{1}H) or chloroform ($\delta = 7.26$ for ^{1}H) as an internal reference unless otherwise stated. ^{13}C NMR spectra were proton decoupled and in $CDCl_3$ with either TMS ($\delta = 0.00$ for ^{13}C) or chloroform ($\delta = 77.0$ for ^{13}C) as an internal reference unless otherwise stated. ^{19}F NMR spectra were referenced to C_6F_6 (-163.0 ppm external). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), app. (apparent) and exch (D_2O exchangeable); coupling constants, *J*, are reported in Hertz (Hz); integration is provided; and assignments of individual resonances are supported in most cases by the following NMR experiments: APT/DEPT, COSY, or HMBC and HMQC. Data are presented in the form: chemical shift (multiplicity, coupling constants, integration and assignments where relevant). Infrared spectra (IR) were recorded KBr pellets on a Mattson Galaxy 5020 spectrometer. Peaks are reported in units of cm^{-1} with the following relative intensities: s (strong, 67 - 100 %), m (medium, 34 - 66 %), w (weak, 0 - 33 %) and br (broad). Mass spectra were obtained through the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. Low-resolution electrospray (ESI) spectra were

obtained on a Quattro spectrometer. Data are reported in the form *m*/*z* (intensity relative to base = 100). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

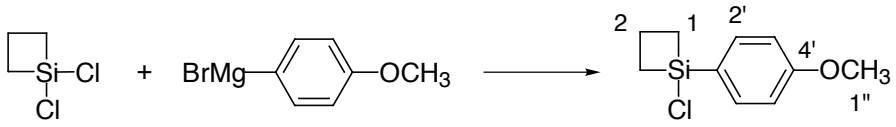
Analytical capillary gas chromatography (GC) was performed using the following gas chromatographs fitted with a flame ionization detector (H_2 carrier gas, 1 mL/min): Hewlett Packard 5890, and Hewlett Packard 5890 Series II. The columns used was HP−5 50−m cross-linked 5 % phenyl methyl silicone gum phase. The injector temperature was 225 °C, the detector temperature was 300 °C. Retention times (t_R) and integrated ratios were obtained from Hewlett Packard 3393A integrators.

The solvents used in reactions were reagent grade and distilled from the indicated drying agents under a nitrogen atmosphere: acetonitrile: CaH_2, tetrahydrofuran (THF) and diethyl ether (Et_2O: sodium metal/benzophenone ketyl. The solvents used for extraction and chromatography were technical grade and distilled from the indicated drying agents: hexane, pentane, dichloromethane (CH_2Cl_2): $CaCl_2$; ethyl acetate (EtOAc): K_2CO_3. Unless otherwise noted, all nonaqueous reactions were performed in oven- and/or flame-dried glassware under an atmosphere of dry nitrogen.

Materials

Tetrabutylammonium fluoride (TBAF) solution in THF (1.0 M) was made from TBAF trihydrate solid bought from Fluka. Tri-*t*-butylphosphine solution in THF (1.0 M) was made from tri-*t*-butylphosphine purchased from Strem. 1,1-Dichlorosilacyclobutane (**1**) was prepared according to literature.[1]

1-Chloro-1-(4'-methoxyphenyl)silacyclobutane (2)



1 **2**

4-Methoxyphenylmagnesium bromide solution in Et_2O was prepared in conventional method and titrated.[2] To a solution of **1** (5.61 g, 39.7 mmol, 1.2 equiv) in Et_2O (80 mL) was added 4-methoxyphenylmagnesium bromide (24.0 mL, 1.38 M, 33.1 mmol) dropwise over 1 h at 0 ˚C. Then the reaction mixture was allowed to warm up to room temperature and was stirred overnight. After Schlenk filtration, all the solvent was removed by simple distillation and the residue was purified by fractional distillation under vacuum to afford 5.21 g (73%) of **2** as a colorless oil.

Analytical data for **2**:

bp: 100 °C (0.1 mmHg)

^{1}H NMR: (500 MHz)

7.69 (d, *J* = 8.6, 2H, HC(2')), 7.02 (d, *J* = 8.6, 2H, HC(3')), 3.88 (s, 3H, HC(1")), 2.37-2.32 (m, 1H, $H_aC(2)$), 2.14-2.08 (m, 1H, $H_bC(2)$), 1.75-1.69 (m, 4H, HC(1))

^{13}C NMR: (125 MHz)

162.06 (C(4')), 135.23 (C(2')), 126.08 (C(1')), 114.22 (C(3')), 55.41 (C(1")), 20.81 (C(1)), 16.35 C(2))

IR: (neat)

2975 (s), 2932 (s), 1594 (s), 1564 (m), 1503 (s), 1462 (m), 1282 (s), 1252 (s), 1183 (s), 1123 (s), 1115 (s), 1030 (s), 852 (s), 824 (s), 693 (s)

MS: (ESI)

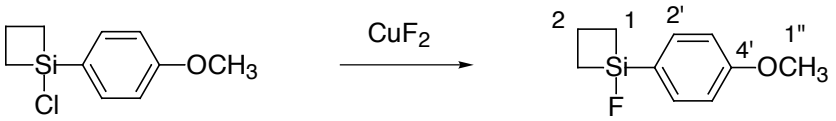
212 (31), 184 (100), 169 (17), 135 (11), 121 (96), 91 (10), 77 (10), 63 (22)

Analysis: $C_{10}H_{13}ClOSi$ (MW 212.75)

Calcd: C, 56.46, H, 6.16, Cl, 16.66

Found: C, 56.19, H, 6.22, Cl, 16.41

1-Fluoro-1-(4'-methoxyphenyl)silacyclobutane (3)



2 **3**

To a solution of **2** (2.98 g, 14.0 mmol) in Et_2O (60 mL) was added CuF_2 (0.71 g, 7.0 mmol, 0.5 equiv) at 0 ˚C. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. The solid was removed by quick filtration through celite and the solvent was distilled off by simple distillation. The residue was then purified by fractional distillation under vacuum to afford 1.98 g (72%) of **3** as a colorless oil.

Analytical data for **3**:

bp: 75 °C (0.1 mmHg)

^{1}H NMR: (500 MHz)

7.61 (d, *J* = 8.6, 2H, HC(2')), 6.98 (d, *J* = 8.6, 2H, HC(3')), 3.84 (s, 3H, HC(1")), 2.19-2.14 (m, 1H, $H_aC(2)$), 1.84-1.77 (m, 1H, $H_bC(2)$), 1.64-1.53 (m, 4H, HC(1))

^{13}C NMR: (125 MHz)

161.85 (C(4')), 134.85 (d, *J* = 2.8, C(2')), 125.09 (d, *J* = 13.8, C(1')), 113.94 (C(3')), 55.11 (C(1")), 19.23 (d, *J* = 12.9, C(1)), 13.32 (d, *J* = 3.6, C(2))

^{19}F NMR: (470 MHz)

148.08 (d, *J* = 6.1)

IR: (neat)

2975 (s), 2947 (s), 2934 (s), 1596 (s), 1564 (m), 1504 (s), 1463 (m), 1400 (m), 1282 (s), 1252 (s), 1181 (s), 1126 (s), 1031 (s), 911 (s), 861 (s), 824 (s), 814 (s), 795 (s), 723 (s), 702 (s)

MS: (ESI)

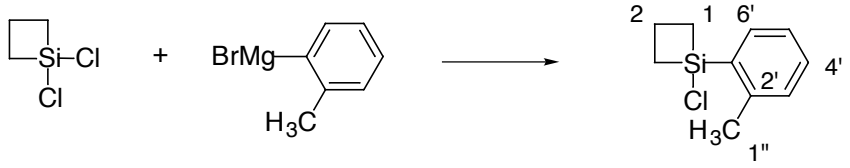
196 (22), 184 (10), 177 (14), 168 (100), 153 (65), 138 (7), 121 (92), 104 (12), 89 (5), 77 (2)

Analysis: $C_{10}H_{13}FOSi$ (MW 196.30)

Calcd: C, 61.19, H, 6.68, F, 9.67

Found: C, 61.28, H, 6.85, F, 9.41

1-Chloro-1-(2'-methylphenyl)silacyclobutane (9)



1 **9**

2-Methylphenylmagnesium bromide was prepared by adding a Et_2O solution (40 mL) of 2-methylbromobenzene (9.89 g, 57.8 mmol) to Mg (1.55 g, 63.58 mmol, 1.1 equiv) over 1 h and refluxing for 2 h. After cooled to room temperature, the resulted solution was added dropwise to a solution of **1** (8.15 g, 57.8 mmol, 1.0 equiv) in Et_2O (80 mL) at 0 ˚C. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. After Schlenk filtration, all the solvent was removed by simple distillation and the residue was purified by fractional distillation under vacuum to afford 8.53 g (78%) of **9** as a colorless oil.

Analytical data for **9**:

bp: 88 °C (0.1 mmHg)

^{1}H NMR: (500 MHz)

7.59 (dd, J = 6.9, 1.3, 1H,), 7.38 (td, J = 7.5, 1.2, 1H), 7.27 (m, 2H), 2.53 (s, 3H, HC(1")), 2.39-2.32 (m, 1H, $H_aC(2)$), 2.12-2.06 (m, 1H, $H_bC(2)$), 1.79-1.69 (m, 4H, HC(1))

^{13}C NMR: (125 MHz)

143.55, 133.89, 133.56, 131.30, 129.98, 125.25, 22.11 (C(1")), 20.23 (C(1)), 16.27 (C(2))

IR: (neat)

2979 (m), 2948 (m), 2931 (m), 2872 (w), 1591 (m), 1478 (m), 1467 (m), 1409 (m), 1389 (w), 1284 (m), 1202 (m), 1133 (s), 1082 (m), 852 (s), 748 (s)

MS: (ESI)

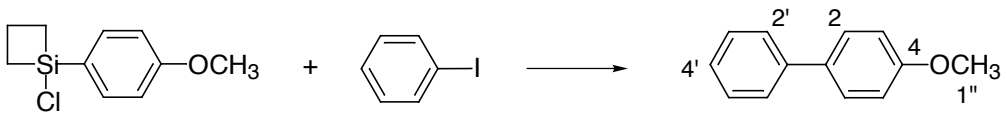
196 (25), 168 (69), 161 (46), 153 (100), 131 (21), 119 (28), 105 (19), 91 (34), 77 (5), 63 (32)

Analysis: $C_{10}H_{13}ClSi$ (MW 196.75)

Calcd: C, 61.05, H, 6.66

Found: C, 60.89, H, 6.88

Palladium Catalyzed Cross-coupling Reaction of Arylsilanes with Aryl Iodides. Representative Procedure: Preparation of 4-Methoxybiphenyl (4)



2 **4**

The reaction of arylsilane **2** and iodobenzene is representative. To the neat **2** (255 mg, 1.2 mmol, 1.2 equiv) was added a solution of tetra *n*-butylammonium fluoride (TBAF) (3.6 ml, 1.0 M in THF, 3.6 mmol, 3.6 equiv). The initial exotherm was allowed to subside

and the solution was stirred until it returned to rt, (ca. 10 min). Iodobenzene (204 mg, 1.0 mmol) was added to the solution followed by tri(*t*-butyl)phosphine (0.2 mL, 1.0 M in THF, 0.2 mmol, 0.2 equiv) and $[allylPdCl]_2$ (9.1 mg, 2.5 mol%). The mixture was heated to reflux for 1 h. After being cooled to rt, the reaction mixture was treated with H_2O (10 mL) and extracted with CH_2Cl_2 (3 X 25 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The crude product was further purified by column chromatography (SiO_2, hexane to hexane/EtOAc,50/1) to afford 0.167 g (91%) of **4** as a white solid. The physical and spectroscopic data matched those in the literature.[3]

Data for **4**:

mp: 90-91 °C

^{1}H NMR: (500 MHz)

7.57-7.52 (m, 4H, HC(2), HC(2')), 7.42 (t, J = 7.8, 2H, HC(3')), 7.31 (t, J = 7.6, 1H, HC(4')), 6.98 (d, J = 6.6, 2H, HC(3)), 3.86 (s, 3H, HC(1"))

GC: t_R, 9.55 min (HP-5, 230 °C, 15 psi)

References

(1) (a) Denmark, S. E.; Griedel, B. D.; Coe, D. M.; Schnute, M. E. *J. Am. Chem. Soc*. **1994**, *116*, 7026. (b) Laane, J. *J. Am. Chem. Soc*. **1967**, *89*, 1144.

(2) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem*. **1967**, *9*, 165.

(3) (a) Tamura, Y.; Chun, M.-W.; Inoue, K.; Minamikawa, J. *Synthesis* **1978**, 822. (b) Lipshutz, B. H.; Siegmann, K.; Garcia, E.; Kayser, F. *J. Am. Chem. Soc*. **1993**, *115*, 9276.