DOI: 10.1002/ejoc.200600589

Remote Trimethylsilyl Groups Interfering with the *ortho* Deprotonation of Fluoroarenes and Chloroarenes

Christophe Heiss,[a] Elena Marzi,[a] Florence Mongin,[b,c] and Manfred Schlosser*[a,c]

Keywords: Acidity / Buttressing effect / Competition kinetics / (Haloaryl)silanes / *ortho*- and *meta*-Metalation

(2-Fluorophenyl)trimethylsilane (**2-F**) and (2-chlorophenyl)trimethylsilane (**2-Cl**) react with *sec*-butyllithium or lithium 2,2,6,6-tetramethylpiperidide under permutational hydrogen/metal interconversion (metalation) more slowly than, respectively, the corresponding 4-fluoro- and 4-chloro isomers (**1-F** and **1-Cl**, respectively) or, on the other hand, fluorobenzene and chlorobenzene themselves. The bulky silyl substituent impedes the neighboring halogen to get out of the way when the base attacks the *ortho* position. For the same reason, (2,4-difluorophenyl)- and (2,4-dichlorophenyl)trimethylsilane (**7-F** and **7-Cl**) are less reactive than their 3,5-isomers (**6-F** and **6-Cl**) and metalation occurs more rapidly at the 4- rather than 3-position of (2,5-difluorophenyl)- and (2,5-dichlorophenyl)trimethylsilane (**5-F** and **5-Cl**, respectively). The decrease in kinetic acidity due to buttressing is most pronounced with the congested substrates (2,4,6-trihalophenyl)trimethylsilanes (**8-F** and **8-Cl**) and, particularly (2,4,6-trihalophenylene)-1,3-bis(trimethylsilanes) (**9-F** and **9-Cl**). Fluorine being far less effective than chlorine as a transmitter of steric pressure, (3,4- and 2,3-difluorophenyl)trimethylsilane (**3-F** and **4-F**) exhibit comparable reactivity whereas (3,4-dichlorophenyl)trimethylsilane (**3-Cl**) clearly surpasses its 2,3-dichloro isomer (**4-Cl**).

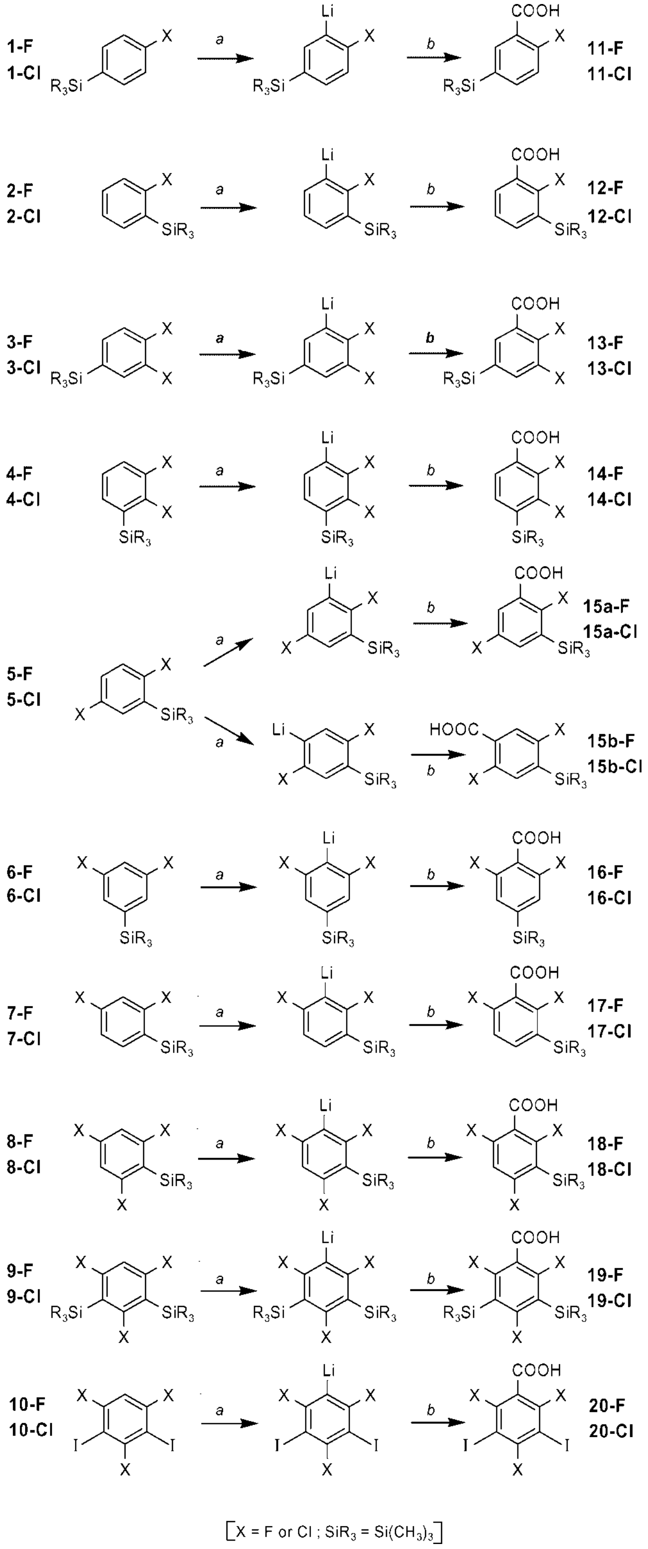
When treated with strongly basic organometallic reagents or metal dialkylamides, (2,6-dichlorophenyl)- and (2,6-dibromophenyl)trialkylsilanes undergo a permutational hydrogen/metal interconversion predominantly if not exclusively at the halogen-remote 4-position ("*meta*-metalation") rather than at the halogen-adjacent 3-position ("*ortho*-metalation").[1,2] Although to varying degrees, a propensity for *meta* metalation was also uncovered with other substrates, in particular 2-fluoro-[3] and 2-trifluoromethyl-[4] substituted phenylsilanes, bromo- or trifluoromethyl-substituted aromatic or heterocyclic substrates[5] and 1,3-dichlorobenzenes carrying relatively small atoms or groups at the 2-position.[6] The phenomenon has been tentatively attributed to buttressing effects operating at the transition state level. According to this hypothesis, steric pressure emanating from an "emitter" group rigidifies the neighboring "transmitter" heterosubstituent, the lone pairs of which cause repulsive electron–electron interactions with the adjacent proton-delivery channel.[5,7] Thus, the proton mobility at the 4-position decreases while that at the 5-position remains unimpaired.

Alternatively, one might assume the 4-position to maintain its ordinary reactivity but be outperformed by the 5-position if the latter is selectively acidified by a still unidentified effect. To rule out this second scenario we have carried out a series of competition experiments juxtaposing fluoro- and chlorotrimethylsilanes with the corresponding silyl-free parent compounds (Scheme 1). More precisely, fluorobenzene, one of the three difluorobenzenes or 1,3,5-trifluorobenzene, chlorobenzene, one of the three dichlorobenzenes or 1,3,5-trichlorobenzene was mixed with its trimethylsilyl-substituted congener (**1-F** through **9-F** or **1-Cl** through **9-Cl**) and the resulting pair of substrates was treated with a stoichiometrically insufficient amount of a strong base, in particular *sec*-butyllithium (LIS) and lithium 2,2,6,6-tetramethylpiperidide (LITMP). The organolithium intermediates were characterized as the corresponding halogenated and silylated benzoic acids (**11-F** through **19-F** and **11-Cl** through **19-Cl**) obtained after trapping with dry ice. The relative rates $k_{\mathrm{rel}}^{\mathrm{corr}}$ with which the (oligo)fluorobenzenes or (oligo)chlorobenzenes and their silylated congeners reacted in the competition experiments followed directly from the substrate concentrations determined before and after the reaction.[8,9]

The metalation of the diiodo compounds **10-F** and **10-Cl**, structural analogs of the bissilanes **9-F** and **9-Cl**, had been reported previously.[10] 1,3,5-Trifluoro-2,4-diiodobenzene was found to react smoothly with lithium *tert*-butyl(*tert*-butyldimethylsilyl)amide (LI^{t}SBA) as evidenced by an almost quantitative conversion into 2,4,6-trifluoro-3,5-

---

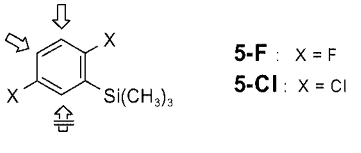
[a] Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale, BCh,
1015 Lausanne, Switzerland
Fax: +41-21-6939365
E-mail: manfred.schlosser@epfl.ch
[b] Institut de Chimie de l'Université 1, (SESO; UMR CNRS 6510),
35042 Rennes, France
[c] Faculté des Sciences, Université, BCh,
1015 Lausanne, Switzerland



Scheme 1. (*a*) Lithiation of (mono-, di- and trihalophenyl)trimethylsilanes using *sec*-butyllithium at –75 °C or lithium 2,2,6,6-tetramethylpiperidide (LITMP) at –100 °C, both in tetrahydrofuran (THF), as the bases; (*b*) carboxylation with dry ice followed by neutralization.

diiodobenzoic acid (**20-F**, isolated in 90% yield) upon carboxylation and neutralization, whereas 1,3,5-dichloro-2,4-diiodobenzene (**10-Cl**) underwent lithiation only sluggishly and provided the 2,4,6-trichloro-3,5-diiodobenzoic acid (**20-Cl**) in a maximum yield of 21%.[10]

The metalation proceeded regioselectively in all cases except one. The substrates **5-F** and **5-Cl**, (2,5-difluorophenyl)- and (2,5-dichlorophenyl)trimethylsilane, were simultaneously metalated at both the 3- and 4-position (Scheme 2). Subsequent carboxylation afforded the acids **15a-F** plus **15b-F** and **15a-Cl** plus **15b-Cl** in 1:3 to 1:5 ratios. Obviously, the attack of the base at the 3-position is compromised by a buttressing effect. No deprotonation at all occurred at the sterically shielded 6-position.



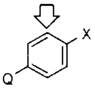
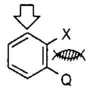
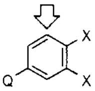
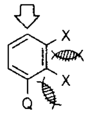
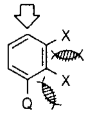
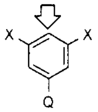
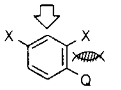
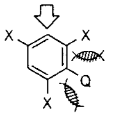
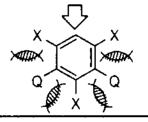
Scheme 2. Concomitant metalation of (2,5-difluorophenyl)trimethylsilane and (2,5-dichlorophenyl)trimethylsilane at the 3- and 4-positions.

To validate the comparison, the experimental k_{rel} values have been statistically corrected by dividing them by the number of equivalent acidic sites thus affording k_{rel}^{corr} values (see Table 1). For example, no correction is warranted in the case of the chlorobenzene/(4-chlorophenyl)trimethylsilane couple as both substrates dispose of two deprotonable *ortho* positions. In contrast, the relative rate of chlorobenzene counts only half when contrasted with that of (2-chlorophenyl)trimethylsilane (**2-Cl**) which has merely one vacant *ortho* position.

Trimethylsilyl groups introduced into remote positions alter the reactivity of a given compound only moderately (Table 1). As one may have predicted on the basis of prior knowledge,[11] they retard the metalation, for example, of (4-halophenyl)trimethylsilanes (**1**) or (3,4-dihalophenyl)trimethylsilanes (**3**) when located *meta* with respect to the deprotonation site, and they accelerate slightly, as in the case of the (3,5-dihalophenyl)trimethylsilanes (**6**), if in *para*. Trimethylsilyl groups reduce the rate substantially when occupying a halogen-neighboring position. In other words, both fluorine and chlorine atoms transmit the steric pressure exerted by a neighboring trialkylsilyl group to the vacant *ortho* position. For obvious reasons,[2,4] the decrease in kinetic acidity is more pronounced in the chloro than in the fluoro series (k_{rel}^{corr} 0.55–0.02 vs. 0.60–0.05, see Table 1) as a comparison of the rates of (2-fluorophenyl)trimethylsilane (**2-F**) and (2-chlorophenyl)trimethylsilane (**2-Cl**) as well as (2,4-difluorophenyl)trimethylsilane (**7-F**) and (2,4-dichlorophenyl)trimethylsilane (**7-Cl**), always relative to the corresponding silyl-free parent compounds, reveals (Table 1).

Although proton abstraction from (2-chlorophenyl)trimethylsilane (**2-Cl**) is slower than from chlorobenzene (see Table 1) it occurs at the 3-position (*"ortho"*) whereas *sec*-butyllithium attacks (2,6-dichlorophenyl)trimethylsilane mainly at the 4-position (*"meta"*).[1,2] Evidently, the silyl group needs to be squeezed in by the two flanking halogen atoms and thus to be buttressed itself to make its but-

Table 1. Competitive reaction between trimethylsilyl-substituted mono-, di- or trifluorobenzenes or mono-, di- or trichlorobenzenes [Q = $Si(CH_3)_3$] and their non-silylated [Q = H] counterparts with *sec*-butyllithium (LIS) or lithium 2,2,6,6-tetramethylpiperidide (LITMP) in tetrahydrofuran at –75 or –100 °C: statistically corrected relative deprotonation rates $k_{rel}^{corr}(= k^{Q = Si(CH_3)_3}/k^{Q = H})$.

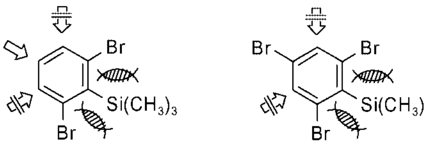
Silane compd. no.	Substrate pair: Q = H and $Si(CH_3)_3$	X = F: k_{rel}^{corr} LIS	X = F: k_{rel}^{corr} LITMP	X = Cl: k_{rel}^{corr} LIS	X = Cl: k_{rel}^{corr} LITMP
1		0.77	1.00	0.63	–
2		0.59	0.29	0.55	–
3		0.67	0.67	0.66	0.78
4		0.77	0.83	0.38	0.40
5		0.22[a] 1.18[b]	0.31[a] 0.97[b]	–	0.23[a] 1.12[b]
6		1.07	1.00	1.25	1.18
7		0.57	0.51	0.24	0.16
8		0.33	0.60	0.30	0.19
9		0.06	0.05	–	0.02

[a] Metalation rate at the 3-position (relative to one fourth of the 1,4-difluorobenzene rate). [b] Metalation rate at the 4-position (relative to one fourth of the 1,4-difluorobenzene rate).

tressing of the halogen located next to the potential deprotonation site effective.

As evidenced by the model compounds (2,3-difluorophenyl)- and (2,3-dichlorophenyl)trimethylsilane (**4-F** and **4-Cl**; Table 1), the transmission of steric pressure through two contiguous halogen atoms is weak in the case of fluorine and substantial in the case of chlorine substituents. As already pointed out with respect to (2-chlorophenyl)- and (2,6-dichlorophenyl)trimethylsilane (see last paragraph of the preceding page) buttressing can become well amplified if an additional *ortho*-halogen atom corners the trimethylsilyl group. Thus, (2,4-difluorophenyl)trimethylsilane (**7-F**; k_{rel}^{corr} 0.57) is considerably more reactive than (2,4,6-trifluorophenyl)trimethylsilane (**8-F**; k_{rel}^{corr} 0.33) toward *sec*-butyllithium. When two silyl substituents are simultaneously introduced into the 1,3,5-trihalobenzene skeleton as this is the case with 2,4,6-trichloro-1,3-phenylenebis(trimethylsilane) (**9-F**) and 2,4,6-trichloro-1,3-phenylenebis(trimethylsilane) (**9-Cl**), the structure is tied up and its reactivity towards bases is drastically diminished (Table 1).

Fluorine and chlorine being known to act as weak and, respectively, moderately strong transmitters of buttressing effects, the present rate studies were intentionally restricted to these two elements as the acidifying substituents. Bromine and iodine would have caused more marked retardations.[5] As one may remember in this context, (2,6-dibromophenyl)trimethylsilane (**11-Br**) undergoes deprotonation no longer at the halogen-adjacent 3-position, but solely at the halogen-remote 4-position[2] and (2,4,6-tribromophenyl)trimethylsilane (**8-Br**) proves to be totally inert even toward the most powerful amide-type bases[10] (Scheme 3).



11-Br **8-Br**

Scheme 3. Selective metalation of (2,6-dibromophenyl)trimethylsilane at the 4-position and no metalation at all of (2,4,6-tribromophenyl)trimethylsilane.

Buttressing effects were first recognized to modulate molecular mobility.[12–16] As our recent studies[1–7] and the present work show, they affect beyond this also chemical reactivity, in particular the kinetic acidity exhibited by aromatic and heterocyclic substrates toward strong bases of the alkyllithium and lithium dialkylamide type. We evidently are dealing with a widespread phenomenon which merits further in-depth experimental and theoretical investigation.

Experimental Section

1. General

Starting materials, if commercial, were purchased from Aldrich-Fluka (9479 Buchs, Switzerland), Acros Organics (2440 Geel, Belgium) and Apollo (SK6 2QR Stockport, Great Britain) and used as such provided that adequate checks (melting ranges, n_D^{20}, gas chromatography) had confirmed the claimed purity. Solutions of butyllithium, *sec*-butyllithium and *tert*-butyllithium in pentanes, hexanes or cyclohexane were supplied by Chemetall (60487 Frankfurt, Germany) and potassium *tert*-butoxide by Callery (Pittsburgh, PA 15230, USA). When known compounds had to be prepared according to literature procedures, pertinent references are given.

Air- and moisture-sensitive materials were stored in Schlenk tubes or Schlenk burettes. They were protected by and handled under 99.995% pure nitrogen, using appropriate glassware (Glasgerätebau Pfeifer, 98711 Frauenfeld, Germany). To render paraffinic or aromatic hydrocarbons (hexanes, toluene) anhydrous, they were submitted to azeotropic distillation. Diethyl ether and tetrahydrofuran were dried by distillation from sodium wire.

If no reduced pressure is specified, boiling ranges (b.p.) refer to ordinary atmospheric conditions (725 ± 25 Torr). The listed melting ranges (m.p.) were found to be reproducible after resolidification, unless stated otherwise ("decomp."), and were corrected using a calibration curve established with authentic standards. If melting points are missing, it means that all attempts had failed to crystallize the liquid or oil at temperatures down to –75 °C. The temperature of dry ice/methanol or dry ice/ethanol baths is consistently indicated as –75 °C and "room temperature" (22–26 °C) as +25 °C.

Whenever possible and appropriate, yields of products were determined, prior to isolation, by gas chromatography comparison of their peak areas with that of a known amount of a reference substance ("internal standard") and corrected by means of separately established calibration factors. Packed columns were made of glass, while quartz was the material selected for capillary columns (>10 m long). In case of programmed temperature increase, a constant rate of 10 °C per minute was applied. The stationary phases employed are encoded as DB-1, OV-17 or SE-30 (of the silicone type), DEGS or DBS (both of the polyester type), Ap-L (Apiezon-L hydrocarbon) and C-20M, DB-Wax or DB-FFAP (all belonging to the polyethylene glycol family).

^{1}H- and ^{13}C-Nuclear magnetic resonance (NMR) spectra of samples dissolved in deuteriochloroform were recorded at 400 and 101 MHz, respectively, or, if marked by an asterisk, at 300 and 75 MHz, respectively. Chemical shifts δ refer to the signal of tetramethylsilane (δ = 0.00 ppm) and coupling constants J are given in Hz. Coupling patterns are, for example, abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), hex (hextet), hep (heptet), oct (octet), non (nonet), td (triplet of doublets) and m (multiplet). Signals of the carboxy hydrogen atoms were not always visible or too broad to be accurately assessed.

Elemental analyses were executed by the laboratory of I. Beetz (96301 Kronach, Germany). The expected percentages were calculated using the atomic weight numbers listed in the 1999 IUPAC recommendations. Further hints concerning working routine, spectra and abbreviations can be found in earlier publications from this laboratory.[3,17–19]

2. Starting Materials and Compounds for Comparison

All halobenzenes (fluorobenzene, the three difluorobenzenes, 1,3,5-trifluorobenzene and the corresponding chloro analogs) employed in the present study are commercially available. The carboxylic acids derived from them by consecutive treatment with an organometallic reagent and dry ice were described previously.[20,21]

a) Silanes

(4-Fluorophenyl)trimethylsilane (1-F): 1-Bromo-4-fluorobenzene (4.9 mL, 8.7 g, 50 mmol) was added to a solution of *tert*-butyllithium (0.10 mol) in pentanes (59 mL) and tetrahydrofuran (0.14 L) cooled in an ethanol/dry ice bath. After 15 min at –75 °C, the reaction mixture was treated with chlorotrimethylsilane (6.3 mL, 5.4 g, 50 mmol). Direct distillation afforded a colorless oil; b.p. 168–170 °C/1 Torr (ref.[22] b.p. 173 °C/1 Torr); n_D^{20} = 1.4723; d_4^{20} = 0.951 (ref.[22] d_4^{20} = 0.9452); yield: 7.40 g (88%). ^{1}H NMR*: δ = 7.49 (dd, J = 8.7, 2.3 Hz, 2 H), 7.05 (t, J = 8.6 Hz, 2 H), 0.28 (s, 9 H) ppm.

(2-Fluorophenyl)trimethylsilane (2-F): Fluorobenzene (4.7 mL, 4.8 g, 50 mmol) was added to a solution of *sec*-butyllithium (50 mmol) in cyclohexane (38 mL) and tetrahydrofuran (70 mL) cooled in an dry ice/ethanol bath. After 45 min at –75 °C, the reaction mixture was treated with chlorotrimethylsilane (6.3 mL, 5.4 g, 50 mmol). Direct distillation afforded a colorless oil; b.p. 170–174 °C/1 Torr (ref.[23] b.p. 167–168 °C/1 Torr); n_D^{20} = 1.4713; d_4^{20} = 0.963; yield: 6.36 g (74%). ^{1}H NMR*: δ = 7.41 (dd, J = 9.0, 7.1 Hz, 1 H), 7.3 (m, 1 H), 7.14 (tt, J = 7.3, 0.9 Hz, 1 H), 6.99 (td, J = 8.6, 0.9 Hz, 1 H), 0.37 (s, 9 H) ppm.

(3,4-Difluorophenyl)trimethylsilane (3-F): Analogously, as described for silane **1-F**, but starting from 1-bromo-3,4-difluorobenzene (5.2 mL, 8.7 g, 50 mmol); colorless oil; b.p. 174–176 °C/1 Torr (ref.[24] 177–178 °C/1 Torr); n_D^{20} = 1.4611; d_4^{20} = 1.156; yield: 7.26 g (78%). ^{1}H NMR*: δ = 7.2 (m, 3 H), 0.18 (s, 9 H) ppm.

(2,3-Difluorophenyl)trimethylsilane (4-F): Analogously, as described for silane **2-F**, but starting from 1,2-difluorobenzene (4.9 mL, 5.7 g, 50 mmol); colorless oil; b.p. 43–45 °C/5 Torr; n_D^{20} = 1.4620; d_4^{20} = 1.130; yield: 8.56 g (92%). ^{1}H NMR*: δ = 7.2 (m, 3 H), 0.38 (s, 9 H) ppm. $C_9H_{12}F_2Si$ (186.28): calcd. C 58.03, H 6.49; found C 58.28, H 5.88.

(2,5-Difluorophenyl)trimethylsilane (5-F): Analogously, as described in the preceding paragraph, from 1,4-difluorobenzene (5.0 mL, 5.7 g, 50 mmol); colorless oil; b.p. 59–61 °C/11 Torr (ref.[25]: b.p. 80–81 °C/35 Torr); n_D^{20} = 1.4504; d_4^{20} = 1.082; yield: 7.92 g (85%). ^{1}H NMR*: δ = 7.1 (m, 3 H), 0.31 (d, J = 0.7 Hz, 9 H) ppm. ^{13}C NMR*: δ = 163.0 (dd, J = 236, 2 Hz), 158.8 (dd, J = 244, 2 Hz), 128.3 (dd, J = 34, 4 Hz), 120.7 (dd, J = 22, 9 Hz), 117.2 (dd, J = 24, 9 Hz), 115.7 (dd, J = 30, 8 Hz), –1.4 (d, J = 1.5 Hz, 3 C) ppm.

(3,5-Difluorophenyl)trimethylsilane (6-F): Analogously, as described for silane **1-F** starting from 1-bromo-3,5-difluorobenzene (12 mL, 19 g, 0.10 mol); colorless oil; b.p. 31–33 °C/5 Torr (ref.[26] b.p. 69–72 °C/20 Torr); n_D^{20} = 1.3780; d_4^{20} = 1.054; yield: 16.6 g (89%). ^{1}H NMR*: δ = 6.98 (symm. m., 2 H), 6.81 (m, 1 H), 0.27 (s, 9 H) ppm.

(2,4-Difluorophenyl)trimethylsilane (7-F): Analogously from 1-bromo-2,4-difluorobenzene (11 mL, 19 g, 0.10 mol); colorless oil; b.p. 37–40 °C/6 Torr (ref.[27] b.p. 73 °C/20 Torr); n_D^{20} = 1.3501; d_4^{20} = 1.049; yield: 16.9 g (91%). ^{1}H NMR*: δ = 7.3 (m, 1 H), 6.86 (td, J = 8.0, 1.9 Hz, 1 H), 6.73 (td, J = 9.2, 2.2 Hz, 1 H), 0.28 (s, 9 H) ppm.

(2,4,6-Trifluorophenyl)trimethylsilane (8-F): Analogously, as described for silane **2-F**, from 1,3,5-trifluorobenzene (7.2 mL, 9.9 g, 75 mmol); colorless oil; b.p. 64–66 °C/2 Torr; n_D^{20} = 1.4458; d_4^{20} = 1.210; yield: 13.6 g (90%). ^{1}H NMR*: δ = 6.56 (dd, J = 9.0, 1.7 Hz, 2 H), 0.36 (t, J = 1.5 Hz, 9 H) ppm. ^{13}C NMR*: δ = 167.6 (dt, J = 238, 20 Hz, 2 C), 164.4 (dt, J = 244, 17 Hz), 109.3 (td, J = 35, 4 Hz), 99.8 (td, J = 32, 8 Hz, 2 C), –0.1 (t, J = 3 Hz, 3 C) ppm. $C_9H_{11}F_3Si$ (204.27): calcd. C 52.92, H 5.43; found C 52.75, H 5.56.

(2,4,6-Trifluoro-1,3-phenylene)bis(trimethylsilylsilane) (9-F): Analogously from (2,4,6-trifluorophenyl)trimethylsilane (see above, 8.3 mL, 10 g, 50 mmol); colorless oil; b.p. 40–42 °C/2 Torr (ref.[24] b.p. 65–66 °C/2 Torr); n_D^{20} = 1.4668; d_4^{20} = 1.166; yield: 9.70 g (70%). ^{1}H NMR*: δ = 6.49 (td, J = 9.2, 1.3 Hz, 1 H), 0.34 (t, J = 0.8 Hz, 18 H) ppm. ^{13}C NMR*: δ = 171.5 (dt, J = 237, 24 Hz), 168.8 (dt, J = 200, 18 Hz, 2 C), 108.9 (td, J = 42, 5 Hz, 2 C), 99.6 (td, J = 31, 7 Hz), 0.3 (t, J = 1.5 Hz, 6 C) ppm.

(4-Chlorophenyl)trimethylsilane (1-Cl): 1-Bromo-4-chlorobenzene (9.6 g, 50 mmol) was added to a solution of butyllithium (50 mmol) in hexanes (30 mL) and diethyl ether (70 mL) cooled in a dry ice/methanol bath. After 15 min at –75 °C, the reaction mixture was treated with chlorotrimethylsilane (6.7 mL, 5.4 g, 50 mmol). Upon immediate distillation, a colorless oil was collected; b.p. 43–45 °C/1 Torr; n_D^{20} = 1.4220; d_4^{20} = 1.034; yield: 8.50 g (92%). ^{1}H NMR: δ = 7.43 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 0.25 (s, 9 H) ppm. ^{13}C NMR: δ = 138.6, 135.1, 134.8 (2 C), 128.0 (2 C), –1.2 (3 C) ppm. $C_9H_{13}ClSi$ (184.74): calcd. C 58.51, H 7.09; found C 58.53, H 7.08.

(2-Chlorophenyl)trimethylsilane (2-Cl): Chlorobenzene (2.5 mL, 2.8 g, 25 mmol) was added to a solution of *sec*-butyllithium (25 mmol) in cyclohexane (40 mL) and tetrahydrofuran (70 mL) at –100 °C. After 2 h at –100 °C, the reaction mixture was treated with chlorotrimethylsilane (3.2 mL, 2.7 g, 25 mmol). Immediate distillation afforded a colorless oil; b.p. 48–50 °C/1 Torr (ref.[28] b.p. = 207–208 °C/740 Torr); n_D^{20} = 1.5126 (ref.[28] n_D^{20} = 1.5121); d_4^{20} = 1.041 (ref.[28] d_4^{20} = 1.026); yield: 3.74 g (81%). ^{1}H NMR: δ = 7.44 (dd, *J* = 7.4, 1.9 Hz, 1 H), 7.32 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.28 (td, *J* = 7.4, 1.6 Hz, 1 H), 7.22 (td, *J* = 7.4, 1.6 Hz, 1 H), 0.37 (s, 9 H) ppm.

(3,4-Dichlorophenyl)trimethylsilane (3-Cl): Analogously, as described for silane **3-F**, but starting from 4-bromo-1,2-dichlorobenzene (13 mL, 23 g, 0.10 mol); colorless oil; b.p.47–49 °C/1 Torr; n_D^{20} = 1.5196; d_4^{20} = 1.224; yield: 19.1 g (87%). ^{1}H NMR*: δ = 7.67 (d, *J* = 1.6 Hz, 1 H), 7.47 (d, *J* = 8.3 Hz, 1 H), 7.39 (dd, *J* = 7.7, 1.3 Hz, 1 H), 0.38 (s, 9 H) ppm. ^{13}C NMR*: δ = 141.1, 135.0, 133.0, 132.4, 132.3, 129.9, –1.4 (3 C) ppm. $C_9H_{12}Cl_2Si$ (219.19): calcd. C 49.32, H 5.52; found C 49.39, H 5.40.

(2,3-Dichlorophenyl)trimethylsilane (4-Cl): Analogously, as described for silane **2-F**, but starting from 1,2-dichlorobenzene (5.6 mL, 7.4 g, 50 mmol); colorless oil; b.p. 39–41 °C/1 Torr; n_D^{20} = 1.5504; d_4^{20} = 1.301; yield: 9.86 g (90%). ^{1}H NMR*: δ = 7.46 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.35 (dd, *J* = 7.4, 1.7 Hz, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 0.39 (s, 9 H) ppm. ^{13}C NMR*: δ = 141.6, 138.4, 133.6, 133.1, 131.3, 127.1, 0.7 (3 C) ppm. $C_9H_{12}Cl_2Si$ (219.19): calcd. C 49.32, H 5.52; found C 49.35, H 5.31.

(2,5-Dichlorophenyl)trimethylsilane (5-Cl): 1,4-Dichlorobenzene (7.4 g, 50 mmol) was added to a solution of *sec*-butyllithium (50 mmol) in cyclohexane (38 mL) and tetrahydrofuran (70 mL) cooled in a dry ice/ethanol bath. After 45 min at –75 °C, chlorotrimethylsilane (6.3 mL, 5.4 g, 50 mmol) was added to the reaction mixture. Direct distillation afforded a colorless oil; b.p. 52–56 °C/1 Torr; n_D^{20} = 1.5321; d_4^{20} = 1.273; yield: 8.87 g (81%). ^{1}H NMR*: δ = 7.39 (t, *J* = 1.1 Hz, 1 H), 7.2 (m, 2 H), 0.38 (s, 9 H) ppm. ^{13}C NMR*: δ = 141.1, 139.0, 135.3, 132.5, 130.5, 130.4, –0.9 (3 C) ppm. $C_9H_{12}Cl_2Si$ (219.19): calcd. C 49.32, H 5.52; found C 49.42, H 5.68.

(3,5-Dichlorophenyl)trimethylsilane (6-Cl): As described for compound **1-Cl**, but starting from 1-bromo-3,5-dichlorobenzene (50 mmol); b.p. 35–37 °C/6 Torr (ref.[29] b.p. 117–123 °C/20 Torr); n_D^{20} = 1.5240; d_4^{20} = 1.220; yield: 10.3 g (94%). ^{1}H NMR: δ = 7.32 (m, 3 H), 0.27 (s, 9 H) ppm.

(2,4-Dichlorophenyl)trimethylsilane (7-Cl): 1-Iodo-2,4-dichlorobenzene (14 g, 50 mmol) was added to a solution of *tert*-butyllithium (0.10 mol) in pentanes (60 mL) and tetrahydrofuran (0.14 L) cooled in a dry ice/methanol bath. After 15 min at –75 °C, the reaction mixture was treated with chlorotrimethylsilane (6.4 mL, 5.4 g, 50 mmol). Immediate distillation afforded a colorless oil; b.p. 31–33 °C/0.8 Torr; n_D^{20} = 1.3161; d_4^{20} = 1.162; yield: 10.2 g (93%). ^{1}H NMR: δ = 7.36 (d, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 1.6 Hz, 1 H), 7.21 (dd, *J* = 8.0, 1.9 Hz, 1 H), 0.35 (s, 9 H) ppm. ^{13}C NMR: δ = 141.5, 136.9, 136.3, 136.0, 129.1, 126.3, –0.9 (3 C) ppm. $C_9H_{12}Cl_2Si$ (219.19): calcd. C 49.32, H 5.52; found C 49.40, H 5.33.

(2,4,6-Trichlorophenyl)trimethylsilane (8-Cl): As described for silane **2-Cl**, but starting from 1,3,5-trichlorobenzene (9.1 g, 50 mmol); colorless oil; was added to the reaction mixture. Direct distillation afforded a colorless oil; b.p. 98–100 °C/1 Torr (ref.[8] b.p. 75–77 °C/0.4 Torr); n_D^{20} = 1.5506; (ref.[8] n_D^{20} = 1.5527); d_4^{20} = 1.307; (ref.[8] d_4^{20} = 1.31); yield: 11.6 g (92%). ^{1}H NMR*: δ = 7.21 (s, 2 H), 0.44 (s, 9 H) ppm.

(2,4,6-Trichloro-1,3-phenylene)bis(trimethylsilane) (9-Cl): 2,2,6,6-Tetramethylpiperidine (8.4 mL, 7.1 g, 50 mmol) and (2,4,6-trichlorophenyl)trimethylsilane (13 g, 50 mmol) were consecutively added to a solution of butyllithium (50 mmol) in hexanes (35 mL) and tetrahydrofuran (70 mL) cooled in a dry ice/ethanol bath. After 2 h at –75 °C, chlorotrimethylsilane (50 mmol) was added to the reaction mixture. Immediate distillation afforded a colorless oil; b.p. 104–106 °C/1 Torr (ref.[30] b.p. 82–84 °C/0.05 Torr); n_D^{20} = 1.5498; d_4^{20} = 1.391; yield: 12.70 g (78%). ^{1}H NMR*: δ = 7.26 (s, 1 H), 0.50 (s, 18 H) ppm. ^{13}C NMR*: δ = 149.3, 142.6 (2 C), 136.3 (2 C), 130.0, 3.6 (6 C) ppm.

3. Carboxylic Acids

All attempts to prepare an authentic sample of 2-chloro-3-(trimethylsilyl)benzoic acid (**12-Cl**) failed. At –100 °C or –75 °C, virtually no metalation occurred and the substrate **2-Cl** was recovered unconsumed.

The methyl esters required for gas chromatographic retention time comparison (see the last Section) were always prepared by treating the benzoic acids described below with an excess of ethereal diazomethane.

2-Fluoro-5-(trimethylsilyl)benzoic Acid (11-F): (4-Fluorophenyl)trimethylsilane (**1-F**; 2.6 mL, 2.5 g, 15 mmol) was added to a solution of *sec*-butyllithium (15 mmol) in cyclohexane (12 mL) and tetrahydrofuran (20 mL) cooled in a dry ice/ethanol bath. After 45 min at –75 °C, the reaction mixture was poured onto freshly crushed dry ice and, when at +25 °C, acidified with 2.0 M hydrochloric acid (10 mL). After extraction with diethyl ether (3 × 15 mL) and evaporation of the combined organic layers, the acid **11-F** crystallized as colorless needles; m.p. 96–98 °C (from hexanes); yield: 2.51 g (79%). ^{1}H NMR*: δ = 8.16 (dd, *J* = 11.2, 8.2 Hz, 1 H), 7.71 (ddd, *J* = 6.9, 5.1, 1.7 Hz, 1 H), 7.14 (dd, *J* = 8.3, 3.0 Hz, 1 H), 0.31 (s, 9 H) ppm. ^{13}C NMR*: δ = 170.3, 163.3 (d, *J* = 264 Hz), 140.6 (d, *J* = 8.8 Hz, 1 H), 137.8, 136.7 (d, *J* = 5 Hz), 117.0 (d, *J* = 8 Hz), 116.6 (d, *J* = 21 Hz), –1.2 (3 C) ppm. $C_{10}H_{13}FO_2Si$ (212.30): calcd. C 56.58, H 6.17; found C 56.65, H 6.19.

2-Fluoro-3-(trimethylsilyl)benzoic Acid (12-F): Prepared analogously from 2-(fluorophenyl)trimethylsilane (**2-F**; 2.6 mL, 2.5 g, 15 mmol); colorless needles; m.p. 142–143 °C (from hexanes); yield: 2.26 g (71%). ^{1}H NMR*: δ = 8.07 (td, *J* = 7.5, 1.7 Hz, 1 H), 7.67 (ddd, *J* = 7.3, 5.3, 2.5 Hz, 1 H), 7.25 (t, *J* = 7.5 Hz, 1 H), 0.31 (s, 9 H) ppm. ^{13}C NMR*: δ = 170.5 (d, *J* = 4 Hz), 166.8 (d, *J* = 256 Hz), 141.0 (d, *J* = 13 Hz), 133.9, 128.5 (d, *J* = 33 Hz), 123.9, 116.8 (d, *J* = 13 Hz), 1.1 (3 C) ppm. $C_{10}H_{13}FO_2Si$ (212.30): calcd. C 56.58, H 6.17; found C 56.38, H 6.04.

2,3-Difluoro-5-(trimethylsilyl)benzoic Acid (13-F): As described for acid **11-F**, but starting from (3,4-difluorophenyl)trimethylsilane (**3-F**; 2.4 mL, 2.8 g, 15 mmol); colorless needles; m.p. 133–135 °C (from hexanes); yield: 2.51 g (90%). ^{1}H NMR*: δ = 7.9 (m, 1 H), 7.53 (ddd, *J* = 9.4, 7.9, 1.9 Hz, 1 H), 0.19 (s, 9 H) ppm. ^{13}C NMR*: δ = 169.5, 150.9 (dd, *J* = 266, 14 Hz), 150.8 (dd, *J* = 253, 12 Hz), 137.7 (dd, *J* = 6, 3 Hz), 132.0 (d, *J* = 3 Hz), 126.9 (d, *J* = 15 Hz), 119.1 (d, *J* = 6 Hz), –1.7 (3 C) ppm. $C_{10}H_{12}F_2O_2Si$ (230.24): calcd. C 52.16, H 5.25; found C 51.73, H 4.95.

2,3-Difluoro-4-(trimethylsilyl)benzoic Acid (14-F): Prepared analogously using the silane **4-F** (2.8 g, 15 mmol) as the starting material; colorless needles; m.p. 150–151 °C (from hexanes); yield: 3.10 g (89%). ^{1}H NMR*: δ = 7.76 (ddd, *J* = 7.7, 6.4, 2.1 Hz, 1 H), 7.22 (ddd, *J* = 5.7, 4.5, 1.5 Hz, 1 H), 0.38 (d, *J* = 0.7 Hz, 9 H) ppm. ^{13}C

NMR*: δ = 169.0 (m), 155.1 (dd, J = 243, 11 Hz), 150.5 (dd, J = 267, 18 Hz), 136.2 (d, J = 26 Hz), 118.8 (dd, J = 10, 5 Hz), 126.6 (d, J = 3 Hz), 119.8 (d, J = 6 Hz), –1.4 (d, J = 1 Hz, 3 C) ppm. $C_{10}H_{12}F_2O_2Si$ (230.29): calcd. C 52.16, H 5.25; found C 52.26, H 5.28.

2,5-Difluoro-4-(trimethylsilyl)benzoic Acid (15b-F): (2,5-Difluorophenyl)trimethylsilane (**5-F**; 3.8 mL, 4.1 g, 15 mmol) was added to a solution of *sec*-butyllithium (15 mmol) in cyclohexane (12 mL) and tetrahydrofuran (20 mL) cooled in a dry ice/ethanol bath. After 45 min at –75 °C, the reaction mixture was poured onto freshly crushed dry ice before being acidified at +25 °C with 2.0 M hydrochloric acid (10 mL). According to gas chromatography (see Section 3), the crude mixture contained 66% of acid **15b-F** and 21% of acid **15a-F**. After extraction with diethyl ether (3 × 15 mL) and evaporation of the combined organic layers, the acid **15b-F** crystallized as tiny colorless needles; m.p. 144–146 °C (from hexanes); yield: 3.07 g (89%). ^{1}H NMR*: δ = 7.60 (dd, J = 7.9, 5.3 Hz, 1 H), 7.17 (dd, J = 10.2, 4.0 Hz, 1 H), 0.35 (d, J = 0.9 Hz, 9 H) ppm. ^{13}C NMR*: δ = 167.9, 162.2 (dd, J = 241, 2 Hz), 158.3 (dd, J = 261, 2 Hz), 137.7 (d, J = 35 Hz), 123.1 (dd, J = 24, 12 Hz), 118.9 (dd, J = 12, 3 Hz), 117.7 (d, J = 31 Hz), –1.5 (d, J = 1.5 Hz, 3 C) ppm. $C_{10}H_{12}F_2O_2Si$ (230.29): calcd. C 52.16, H 5.25; found C 52.17, H 5.28. The isomeric **2,5-difluoro-3-(trimethylsilyl)benzoic acid (15a-F)** was isolated from the mother liquors by sublimation; colorless needles (from hexanes); m.p. 88–89 °C; yield: 0.52% (15%). ^{1}H NMR: δ = 7.68 (ddd, J = 8.0, 5.5, 3.5 Hz, 1 H), 7.31 (dt, J = 7.1, 3.5 Hz, 1 H), 0.36 (d, J = 0.9 Hz, 9 H) ppm. $C_{10}H_{12}F_2O_2Si$ (230.29): calcd. C 52.16, H 5.25; found C 52.11, H 5.18.

2,6-Difluoro-4-(trimethylsilyl)benzoic Acid (16-F): Analogously, as described above for acid **11-F**, from (3,5-difluorophenyl)trimethylsilane (**6-F**; 4.7 g, 25 mmol); colorless needles; m.p. 105–107 °C (from hexanes); yield: 5.29 g (92%). ^{1}H NMR*: δ = 7.09 (d, J = 8.0 Hz, 2 H), 0.30 (s, 9 H) ppm. ^{13}C NMR*: δ = 167.5 (s), 160.6 (dd, J = 262, 5 Hz, 2 C), 150.3 (t, J = 5 Hz), 116.3 (symm. m), 109.3 (t, J = 16 Hz, 2 C), 1.8 (3 C) ppm. $C_{10}H_{12}F_2O_2Si$ (230.29): calcd. C 52.16, H 5.25; found C 52.28, H 5.24.

2,6-Difluoro-3-(trimethylsilyl)benzoic Acid (17-F): As described above for acid **11-F**, but starting from (2,4-difluorophenyl)trimethylsilane (4.7 g, 25 mmol); colorless needles; m.p. 98–100 °C (from hexanes); yield: 5.07 g (88%). ^{1}H NMR: δ = 7.50 (dt, J = 6.4, 1.6 Hz, 1 H), 6.97 (td, J = 6.7, 1.6 Hz, 1 H), 0.35 (t, J = 1.5 Hz, 9 H) ppm. ^{13}C NMR*: δ = 168.0, 165.0 (dd, J = 251, 5 Hz), 162.2 (dd, J = 260, 6 Hz), 138.9 (dd, J = 15, 5 Hz), 123.0 (dd, J = 32, 4 Hz), 112.0 (dd, J = 21, 4 Hz), 109.3 (dd, J = 15, 5 Hz), –1.2 (3 C) ppm. $C_{10}H_{12}F_2O_2Si$ (230.29): calcd. C 52.16, H 5.54; found C 51.89, H 5.19.

2,4,6-Trifluoro-3-(trimethylsilyl)benzoic Acid (18-F): Prepared, analogously as described above for acid **11-F**, from silane **8-F** (2.6 mL, 3.1 g, 15 mmol); colorless needles; m.p. 76–77 °C (from hexanes); yield: 2.56 g (69%). ^{1}H NMR: δ = 6.69 (ddd, J = 10.3, 8.7, 1.7 Hz, 1 H), 0.39 (t, J = 1.5 Hz, 9 H) ppm. ^{13}C NMR: δ = 167.2 (ddd, J = 251, 20, 5 Hz), 166.8 (s), 165.7 (ddd, J = 205, 17, 8 Hz), 162.9 (ddd, J = 212, 16, 8 Hz), 111.0 (td, J = 36, 4 Hz), 106.2 (ddd, J = 19, 16, 6 Hz), 100.9 (ddd, J = 31, 4, 2 Hz), –1.7 (t, J = 3 Hz, 3 C) ppm. $C_{10}H_{11}F_3O_2Si$ (248.28): calcd. C 48.38, H 4.47; found C 48.17, H 4.21.

2,4,6-Trifluoro-3,5-bis(trimethylsilyl)benzoic Acid (19-F): Prepared, analogously as described above for acid **11-F**, from silane **9-F** (3.5 mL, 4.1 g, 15 mmol); colorless needles; m.p. 153–155 °C (from hexanes); yield: 2.70 g (56%). ^{1}H NMR*: δ = 0.37 (s) ppm. ^{13}C NMR*: δ = 172.8 (dt, J = 246, 30 Hz), 167.7, 167.0 (dt, J = 255, 21 Hz, 2 C), 110.3 (td, J = 24, 3 Hz), 105.7 (td, J = 21, 5 Hz, 2 C), –1.5 (t, J = 3 Hz, 6 C) ppm. $C_{13}H_{19}F_3O_2Si_2$ (320.46): calcd. C 48.72, H 5.98; found C 48.79, H 6.04.

2-Chloro-5-(trimethylsilyl)benzoic Acid (11-Cl): Prepared, analogously as described above for acid **11-F**, from (4-chlorophenyl)trimethylsilane (**1-Cl**; 2.8 mL, 2.8 g, 15 mmol); tiny colorless needles; m.p. 78–80 °C; yield: 2.45 g (72%). ^{1}H NMR: δ = 8.12 (d, J = 1.6 Hz, 1 H), 7.60 (dd, J = 7.9, 1.6 Hz, 1 H), 7.47 (d, J = 8.0 Hz, 1 H), 0.30 (s, 9 H) ppm. ^{13}C NMR: δ = 171.7, 139.6, 138.7, 137.2, 135.3, 130.7, 127.8, –1.4 (3 C) ppm. $C_{10}H_{13}ClO_2Si$ (228.75): calcd. C 52.51, H 5.73; found C 52.53, H 5.80.

2,3-Dichloro-5-(trimethylsilyl)benzoic Acid (13-Cl): Prepared, analogously as described above for acid **11-F**, from (3,4-dichlorophenyl)trimethylsilane (**3-Cl**; 2.7 mL, 3.3 g, 15 mmol); tiny colorless needles; m.p. 166–168 °C (from hexanes); yield: 3.35 g (85%). ^{1}H NMR: δ = 7.95 (d, J = 1.5 Hz, 1 H), 7.75 (d, J = 1.5 Hz, 1 H), 0.33 (s, 9 H) ppm. ^{13}C NMR: δ = 170.2, 141.2, 138.7, 134.7, 134.6, 132.8, 130.4, –1.4 (3 C) ppm. $C_{10}H_{12}Cl_2O_2Si$ (263.20): calcd. C 45.64, H 4.60; found C 45.15, H 4.52.

2,3-Dichloro-4-(trimethylsilyl)benzoic Acid (14-Cl): Prepared, analogously as described above for acid **11-F**, from (2,3-dichlorophenyl)trimethylsilane (**4-Cl**; 3.3 g, 15 mmol); tiny colorless needles; m.p. 121–123 °C (from hexanes); yield: 3.39 g (86%). ^{1}H NMR*: δ = 7.81 (d, J = 7.7 Hz, 1 H), 7.45 (d, J = 7.5 Hz, 1 H), 0.37 (s, 9 H) ppm. ^{13}C NMR*: δ = 170.9, 146.8, 140.8, 133.0, 132.5, 131.4, 129.0, –0.91 (3 C) ppm. $C_{10}H_{12}Cl_2O_2Si$ (263.20): calcd. C 45.64, H 4.60; found C 45.46, H 4.40.

2,5-Dichloro-4-(trimethylsilyl)benzoic Acid (15b-Cl): Prepared, analogously as described above for acid **11-F**, from (2,5-chlorophenyl)trimethylsilane (**5-Cl**; 2.6 mL, 3.3 g, 15 mmol); tiny colorless needles; m.p. 114–116 °C (from hexanes); yield: 2.68 g (68%). ^{1}H NMR*: δ = 7.97 (s, 1 H), 7.53 (s, 1 H), 0.41 (s, 9 H) ppm. ^{13}C NMR*: δ = 169.2, 146.7, 139.0, 138.2, 132.5, 129.6, –1.2 (s, 3 C) ppm. $C_{10}H_{12}Cl_2O_2Si$ (263.20): calcd. C 45.69, H 4.61; found C 45.57, H 4.50. – According to gas chromatography (see Section 3), the crude reaction mixture contained 74% of acid **15b-Cl** and 15% of acid **15a-Cl**. A 1: 1 composition isolated from mother liquors enabled the structural assignment of the minor component **15a-Cl**. ^{1}H NMR: δ = 7.88 (d, J = 0.6 Hz, 1 H), 7.56 (d, J = 0.7 Hz, 1 H), 0.41 (s, 9 H) ppm.

2,6-Dichloro-4-(trimethylsilyl)benzoic Acid (16-Cl): Prepared, analogously as described above for acid **11-F**, from (3,5-dichlorophenyl)trimethylsilane (**6-Cl**; 5.5 g, 25 mmol); colorless needles; m.p. 160–162 °C (from hexanes); yield: 5.92 g (92%). ^{1}H NMR*: δ = 7.43 (s, 2 H), 0.30 (s, 9 H) ppm. ^{13}C NMR*: δ = 170.4, 146.6, 132.3 (2 C), 132.1 (2 C), 131.3, –1.5 (3 C) ppm. $C_{10}H_{12}Cl_2O_2Si$ (263.20): calcd. C 45.64, H 4.60; found C 45.57, H 4.50.

2,6-Dichloro-3-(trimethylsilyl)benzoic Acid (17-Cl): Prepared, analogously as described above for acid **11-F**, from (2,4-dichlorophenyl)trimethylsilane (**7-Cl**; 5.5 g, 25 mmol). Extraction with hexanes (3 × 25 mL), evaporation of the combined organic layers and crystallization of the residue from hexanes (10 mL) afforded colorless needles; m.p. 152–154 °C; yield: 5.79 g (88%). ^{1}H NMR*: δ = 7.44 (d, J = 8.3 Hz, 1 H), 1.33 (d, J = 8.3 Hz, 1 H), 0.38 (3 C) ppm. ^{13}C NMR*: δ = 171.1, 138.6, 137.3, 137.0, 132.8, 132.3, 127.1, –1.0 (3 C) ppm. $C_{10}H_{12}Cl_2O_2Si$ (263.20): calcd. C 45.64, H 4.60; found C 45.66, H 4.47.

2,4,6-Trichloro-3-(trimethylsilyl)benzoic Acid (18-Cl): Prepared, analogously as described above for acid **11-F**, from silane **8-Cl** (3.5 mL, 4.1 g, 15 mmol); colorless needles; m.p. 112–114 °C (from hexanes); yield: 4.06 g (91%). ^{1}H NMR*: δ = 7.40 (s, 1 H), 0.54 (s, 9 H) ppm. ^{13}C NMR*: δ = 169.0, 143.1, 138.1, 136.9, 132.3, 132.1, 129.2, 128.2, 2.8 (3 C) ppm. $C_{10}H_{11}Cl_3O_2Si$ (297.64): calcd. C 40.35, H 3.73; found C 40.32, H 4.00.

2,4,6-Trichloro-3,5-bis(trimethylsilyl)benzoic Acid (19-Cl): 2,2,6,6-Tetramethylpiperidine (15 mmol) and the silane **9-Cl** (4.9 g, 15 mmol) were consecutively added to a solution of butyllithium (15 mmol) in hexanes (15 mL) and tetrahydrofuran (20 mL) cooled to –100 °C. After 2 h at –100 °C, the reaction mixture was poured onto freshly crushed dry ice. The reaction mixture was worked up as described for acid **17-Cl**; colorless needles; m.p. 214–216 °C (from hexanes); yield: 3.94 g (71%). ^{1}H NMR*: δ = 0.52 (s) ppm. ^{13}C NMR*: δ = 170.5, 149.9, 138.2 (2 C), 137.5 (2 C), 133.1, 3.5 (6 C) ppm. $C_{13}H_{11}Cl_3O_2Si_2$ (369.82): calcd. C 42.22, H 5.18; found C 48.02, H 5.17.

4. Competition Kinetics

The method as such has already been described in great detail.[10,11,20,21,31,32] Thus, further indications can be restricted to a few specific issues.

Pairs of substrates (approx. 5 mmol each) and a reference compound for quantification (approx. 1 mmol) were dissolved in tetrahydrofuran (15 mL) and analyzed by gas chromatography (2 m, 10% Bentone-34, 50 °C [15 min]→140 °C [40 min; heating rate 10 °C/min]; 60 m BGB-2.5, 60 °C [30 min]→200 °C [20 min; heating rate 30 °C/min]) before *sec*-butyllithium (5.0 mmol) in cyclopentane (3.5 mL) or lithium 2,2,6,6-tetramethylpiperidide (from 5.0 mmol 2,2,6,6-tetramethylpiperidine and 5.0 mmol butyllithium) in hexanes (3.5 mL) was added. After 15 min at –100 °C, the mixture was poured onto freshly crushed dry ice. Once the excess of carbon dioxide had been slowly evaporated, a 1.0 M aqueous solution (10 mL) of sodium hydroxide and, as a second "internal standard", benzoic acid (approx. 1 mmol) were added. The unconsumed substrates and the standard were extracted with diethyl ether (3 × 10 mL) and their concentrations determined by gas chromatography (conditions: see above). The aqueous phase was acidified to pH 1 and then extracted also with diethyl ether (3 × 10 mL). The combined organic layers were treated with ethereal diazomethane until persistence of the yellow color. The relative concentrations of the methyl esters were again determined by gas chromatography (30 m, DB-1, 100 °C; 30 m, DB-Wax, 100 °C) using separately established calibration factors for correction of the response ratios. The amounts of the methyl esters identified in this way coincided with the amounts of the corresponding substrates consumed in the experiment within reasonable limits of errors (max. ±5%).

Acknowledgments

This work was supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Bern (grant 20-100′336-02).

---

[1] C. Heiss, E. Marzi, M. Schlosser, *Eur. J. Org. Chem.* **2003**, 4625–4629.
[2] C. Heiss, F. Cottet, M. Schlosser, *Eur. J. Org. Chem.* **2005**, 5236–5241.
[3] C. Heiss, F. Leroux, M. Schlosser, *Eur. J. Org. Chem.* **2005**, 5242–5247.
[4] M. Schlosser, C. Heiss, F. Leroux, *Eur. J. Org. Chem.* **2006**, 735–737.
[5] M. Schlosser, F. Cottet, C. Heiss, O. Lefebvre, M. Marull, E. Masson, R. Scopelliti, *Eur. J. Org. Chem.* **2006**, 729–734.
[6] M. Schlosser, C. Heiss, E. Marzi, R. Scopelliti, *Eur. J. Org. Chem.* **2006**, 4398–4404.
[7] J. Gorecka, C. Heiss, R. Scopelliti, M. Schlosser, *Org. Lett.* **2004**, *6*, 4591–4593.
[8] C. K. Ingold, F. R. Shaw, *J. Chem. Soc.* **1927**, 2918–2929.
[9] M. Schlosser, V. Ladenberger, *Chem. Ber.* **1967**, *100*, 3901–3915.
[10] F. Mongin, E. Marzi, M. Schlosser, *Eur. J. Org. Chem.* **2001**, 2771–2777.
[11] M. Schlosser, J. H. Choi, S. Takagishi, *Tetrahedron* **1990**, *46*, 5633–5648.
[12] S. L. Chien, R. Adams, *J. Am. Chem. Soc.* **1934**, *56*, 1787–1792.
[13] G. B. Kistiakowsky, W. R. Smith, *J. Am. Chem. Soc.* **1936**, *58*, 1043–1045.
[14] F. H. Westheimer, in *Steric Effects in Organic Chemistry* (Ed.: M. S. Newman), Wiley, New York, **1956**, pp. 523–555, spec. 552–554.
[15] W. Theilacker, R. Hopp, *Chem. Ber.* **1959**, *92*, 2293–2301.
[16] L. A. Paquette, J. M. Gardlik, *J. Am. Chem. Soc.* **1980**, *102*, 5033–5035.
[17] M. Schlosser, M. Marull, *Eur. J. Org. Chem.* **2003**, 447–451.
[18] E. Masson, M. Schlosser, *Eur. J. Org. Chem.* **2005**, 4401–4405.
[19] F. Leroux, O. Lefebvre, M. Schlosser, *Eur. J. Org. Chem.* **2006**, 3147–3151.
[20] M. Schlosser, E. Marzi, F. Cottet, H. H. Büker, N. M. M. Nibbering, *Chem. Eur. J.* **2001**, *7*, 3511–3516.
[21] E. Marzi, M. Schlosser, *Chem. Eur. J.* **2005**, *11*, 3449–3454.
[22] J. D. Roberts, E. A. McElhill, R. Armstrong, *J. Am. Chem. Soc.* **1949**, *71*, 2923–2926.
[23] F. Effenberger, W. Daub, *Chem. Ber.* **1991**, *124*, 2113–2118.
[24] T. D. Yarwood, A. J. Waring, P. L. Coe, *J. Fluorine Chem.* **1996**, *78*, 113–119.
[25] S. S. Dua, H. Gilman, *Indian J. Chem., Sect B* **1979**, *17*, 562–565.
[26] P. A. Deck, C. L. Beswick, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 1772–1784.
[27] P. Babin, B. Bennetau, M. Theurig, J. Dunoguès, *J. Organomet. Chem.* **1993**, *446*, 135–138.
[28] I. Haiduc, H. Gilman, *J. Organomet. Chem.* **1968**, *13*, P4–P6.
[29] D. Wrobel, U. Wannagat, *J. Organomet. Chem.* **1982**, *225*, 203–210.
[30] I. Haiduc, H. Gilman, *J. Organomet. Chem.* **1968**, *12*, 394–396.
[31] F. Faigl, E. Marzi, M. Schlosser, *Chem. Eur. J.* **2000**, *6*, 771–777.
[32] E. Castagnetti, M. Schlosser, *Chem. Eur. J.* **2002**, *8*, 799–804.

Received: July 11, 2006