ELECTRONIC EFFECTS AND THE STEREOCHEMISTRIES IN REARRANGEMENT-DISPLACEMENT REACTIONS OF TRIARYL(HALOMETHYL)SILANES WITH FLUORIDE AND WITH ALKOXIDE IONS

John M. Allen*, Steve L. Aprahamian‡, Esther A. Sans‡, and Harold Shechter*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

SUPPORTING INFORMATION

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Migratory Aptitudes of the p-Cl-Ph and the p-(CH$_2$)$_2$N-Ph Groups, Respectively, in Rearrangement-Displacement Reactions of 14b and 14f at 23 °C in THF with TBAF in Varied Concentrations.

In the Results and Discussion of the present study, the effects of concentration of fluoride ion in rearrangement-displacements of 14b and of 14f in THF at 23 °C were summarized and discussed. In these experiments the conditions were varied by adding the (bromomethyl)silane all at once to the TBAF in different concentrations in THF at 23 °C. The experimental details and the migratory aptitudes found for the p-Cl-Ph and the p-(CH$_2$)$_2$N-Ph groups in reactions of 14b and of 14f at 23 °C are summarized in Table S-1. As has been indicated previously, increasing the F$^-$ concentration in reactions of 14b from 0.095 M to 2.44 M causes little change in the migratory aptitude of the p-chlorophenyl group. Increasing the TBAF concentrations from 0.004 to 2.44 molar in reactions of 14b however result in an increase in the migratory aptitude of the p-dimethylaminophenyl group from 1.23 to 1.51. The increase in the migratory aptitude of the p-(CH$_2$)$_2$N-Ph group led to the further studies that are reported in the Results and Discussion of the present study.

Table S1. Migratory Aptitudes of the p-Cl-Ph and the p-(CH$_2$)$_2$N-Ph Groups, Respectively, in Rearrangement-Displacements of 14b and 14f at 23 °C in THF with TBAF in Varied Concentrations.

<table>
<thead>
<tr>
<th>Silane 14b, p-Cl-Ph-</th>
<th>TBAF, molarity</th>
<th>Corrected (p-Z-Ph/Ph)</th>
<th>Silane 14f, p-(CH$_2$)$_2$N-Ph-</th>
<th>TBAF, molarity</th>
<th>Corrected (p-Z-Ph/Ph)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14b</td>
<td>0.095</td>
<td>1.80</td>
<td>14f</td>
<td>0.0040</td>
<td>1.23</td>
</tr>
<tr>
<td>14b</td>
<td>0.19</td>
<td>1.86</td>
<td>14f</td>
<td>0.043</td>
<td>1.26</td>
</tr>
<tr>
<td>14b</td>
<td>2.44</td>
<td>1.82</td>
<td>14f</td>
<td>0.087</td>
<td>1.37</td>
</tr>
<tr>
<td>14f</td>
<td></td>
<td></td>
<td>14f</td>
<td>0.14</td>
<td>1.33</td>
</tr>
<tr>
<td>14f</td>
<td></td>
<td></td>
<td>14f</td>
<td>0.26</td>
<td>1.33</td>
</tr>
<tr>
<td>14f</td>
<td></td>
<td></td>
<td>14f</td>
<td>2.44</td>
<td>1.51(1.63)$^a$</td>
</tr>
</tbody>
</table>

$^a$ The migratory aptitude from reaction of 14f with CsF (9.5 equiv) in THF at 23 °C.

S7
The Optical Behaviors of (+)-(Bromomethyl)-1-naphthylphenylsilane[(+)-23] with Varied Equivalents of TBAF.

As has been reported in the Results and Discussions of the present investigation experiments have been conducted with excess (+)-23 and TBAF (eq 7) in which the reaction times, exposure of the 51 and 52 formed to F, and handling of the reaction mixtures were greatly minimized. The optical properties of the 51 formed were then estimated very quickly without separating the products. Reactions were conducted in 5-10 min in THF at 23 °C in which the equivalents of (+)-23 ([δ]D23 + 8.29 °, cyclohexane) to TBAF ranged from 1.0 to 0.25-0.98 [the (+)-23 was always in excess] as in Table S-2 and the solutions were then rapidly filtered, quickly diluted to volume, and their optical rotations immediately determined without further workup. In these experiments, because the migratory aptitudes of the phenyl and the 1-naphthyl groups are ~10.4:1 in reactions of (+)-23 with TBAF at 23 °C, the amounts of 52 formed are very small compared to 51 and the 52 will have little effect on the optical activities of the solutions of the product mixtures. Also, prior to determination of the optical rotation of each reaction mixture, cleavages of 51 and 52 by TBAF/H2O to toluene (21) and difluoro(methyl)-1-naphthylsilane[(1-Np)(CH3)SiF2] and to 1-methylnaphthalene (CH3-1-Np) and difluoro(methyl)phenylsilane...

Table S2. Optical Behaviors of Solutions from Reactions of (+)-23 ([α]D22 + 8.29°, cyclohexane) with Varied Equivalents of TBAF in THF at 23 °C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(+)-23a mmol</th>
<th>TBAF mmol</th>
<th>TBAF equiv</th>
<th>bObserved Rotation, αD</th>
<th>% Optical Activity Retained</th>
<th>% Excess (+)-23c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.184</td>
<td>0.00</td>
<td>0.00</td>
<td>+0.461°</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>0.184</td>
<td>0.046</td>
<td>0.25</td>
<td>+0.320°</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>0.182</td>
<td>0.091</td>
<td>0.50</td>
<td>+0.197°</td>
<td>43</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>0.186</td>
<td>0.14</td>
<td>0.75</td>
<td>+0.102°</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>0.184</td>
<td>0.18</td>
<td>0.98</td>
<td>+0.083°</td>
<td>18</td>
<td>2</td>
</tr>
</tbody>
</table>

a [α]D22 + 8.29°. b The optical rotation of each reaction mixture diluted to one mL in THF. c The hypothetical percentage of the initial (+)-23 remaining in solution on the basis that the TBAF reacts totally with (+)-23 by rearrangement-displacements.
[Ph(CH₂)SiF₃], respectively, occur to a small extent which removes F⁻ and leads to further unreacted (+)-23. These experiments are described further and discussed as follows.

Table S-2 reveals that, as the initial equivalents of TBAF to (+)-23 (δ = 8.29 °C, cyclohexane) increase to ~ 1:1 (experiments 1-5), the optical rotations of the reaction mixtures decrease quickly and remain positive. In experiments 2-4 (Table S-2) in which the initial percentages of the equivalents of TBAF to (+)-23 are 25, 50, and 75%, respectively, the optical activities of the reaction solutions correspond to that as 70, 43, and 22%, respectively, of the initial (+)-23 remained. Chromatography of the reaction mixture from experiment 2, Table S-2, then results in isolation of a major solid which ¹H NMR shows to be 85% initial (bromomethyl)silane (+)-23 and 15% rearrangement-displacement product 51. When the initial ratio of the equivalents of (+)-23 to TBAF is 1.00:0.98 (experiment 5), 18% of the initial optical activity of the solution of (+)-23 remains. Rapid workup of the reaction solution from experiment 5 including chromatography on silica gel then yields a major solid product which by ¹H NMR is a mixture of 23 (27.5%) and 51 (72.5%). The experiments summarized in Table S-2 and as concluded in the Results and Discussion show that the optical rotations of the reaction mixtures before any workup correspond quite well to the (+)-23 predicted to be present and the contributions of 51 to the optical activities are non-existent or at best small.

**Experimental Procedures or Directions for Synthesis of Silanes 13a-f, 29b-e, 14d-e, 15b-f, 17b (Z-p-Cl), 17b (Z-p-CH₂), 20b (Z-p-Cl), 20b (Z-p = H), 20b (Z-p-CH₃), 28a, and 30, Respectively.**

**(Chloromethyl)diphenyl(p-trifluoromethyl)phenyl)silane (13a).** Prepared from 26 and 27 (Z-p = CF₃) by Procedure B: white needles (51%); mp 98-100 °C; ¹H NMR (CDCl₃) δ 7.65-7.20 (m, 14H), 3.45 (s, 2H); exact mass calcd for CₙH₁₄F₃Si [M⁺ - (CH₂Cl)] m/e 327.0817, found 327.0802. Anal. Calcd for C₂₀H₁₆ClF₃Si: C, 63.74; H, 4.25. Found: C, 64.00; H, 4.29.

**(Chloromethyl)(p-chlorophenyl)diphenylsilane (13b).** Obtained from 26 and 27 (Z-p = Cl) by Procedure B: white needles (54%); mp 84-85 °C; ¹H NMR (CDCl₃) δ 7.60-7.20 (m, 14H),
3.40 (s, 2H); exact mass calcd for $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{Si} [M^+ - (\text{CH}_2\text{Cl})]$ m/e 342.0400, found 342.0424.

Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{Si}$: C, 66.47; H, 4.66. Found: C, 65.99; H, 4.64.

**Chloromethyl)(p-methylphenyl)diphenylsilane (13d).** Synthesized from 26 and 27 (Z-$p = \text{CH}_3$) by Procedure A: white needles (54%); mp 76-79 °C; $^1\text{H NMR (CDCl}_3\text{)} \delta 7.60-7.05$ (m, 14H), 3.40 (s, 2H), 2.40 (s, 3H); exact mass calcd for $\text{C}_{19}\text{H}_{17}\text{Si} (M^+ - \text{CH}_2\text{Cl})$ m/e 273.1100, found 273.1096. Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{ClSi}$: C, 74.42; H, 5.89. Found: C, 74.73; H, 5.95.

**Chloromethyl)(p-methoxyphenyl)diphenylsilane (13e).** Prepared from 26 and 27 (Z-$p = \text{OCH}_3$) by Procedure B, vacuum distillation, and crystallization: white needles (30%); mp 60-62 °C; $^1\text{H NMR (CDCl}_3\text{)} \delta 7.65-6.80$ (m, 14H), 3.80 (s, 3H), 3.40 (s, 2H); exact mass calcd for $\text{C}_{20}\text{H}_{19}\text{ClO}_2\text{Si}$ m/e 338.0895, found 338.0907. Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{ClSi}$: C, 70.90; H, 5.61. Found: C, 71.21; H, 5.52.

**Chloromethyl)(p-dimethylamino)phenyl)diphenylsilane (13f).** Obtained from 26 and 27 (Z-$p = \text{OCH}_3$) by Procedure A: white needles (30%); mp 106-110 °C; $^1\text{H NMR (CDCl}_3\text{)} \delta 7.55-6.55$ (m, 14H), 3.40 (s, 2H), 2.95 (s, 6H); exact mass calcd for $\text{C}_{21}\text{H}_{22}\text{ClN}_2\text{Si}$ m/e 351.1213, found 351.1163. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{ClN}_2\text{Si}$: C, 71.69; H, 6.26. Found: C, 71.49; H, 6.23.

**p-Chlorophenyl)(dibromomethyl)diphenylsilane (29b).** Prepared from (p-chlorophenyl)diphenylsilane (28b) as in Procedure D: white crystals (42%); mp 116.5-118 °C; $^1\text{H NMR (CDCl}_3\text{)} \delta 7.75-7.35$ (m, 14H), 5.73 (s, 1H); MS (no $M^+$ was observed) 293.0563 (C$_{18}$H$_{14}$ClSi, 100%). Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{Br}_2\text{ClSi}$: C, 48.90%; H, 3.24%. Found: C, 48.88%; H, 3.24%.

**Dibromomethyl)(triphenylsilane (29c).** Synthesized from triphenylsilane (28c) as in Procedure D: white crystals (30%); mp 148-152 °C, lit.$^8$ mp 154-156 °C.

**Dibromomethyl)(p-methylphenyl)diphenylsilane (29d).** Obtained from (p-methylphenyl)diphenylsilane (28d) as in Procedure D: white crystals (53%); mp 110-112 °C; $^1\text{H NMR (CDCl}_3\text{)} \delta 7.80-7.32$ (m, 12H), 7.25-7.22 (d, 2H), 5.75 (s, 1H), 2.40 (s, 3H).

**Dibromomethyl)(p-methoxyphenyl)diphenylsilane (29e).** Synthesized from (p-methoxyphenyl)diphenylsilane (28e) as in Procedure D: white crystals (58%); mp 124-127 °C;
\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.72-7.37 (m, 12H), 6.98-6.94 (d, 2H), 5.74 (s, 1H), 3.84 (s, 3H); MS (no M* was found) 289.1049 (C\(_{19}\)H\(_{17}\)SiO, 100%). Anal. Calcd for C\(_{20}\)H\(_{19}\)BrOSi: C, 51.97%; H, 3.92%. Found: C, 51.84%; H, 3.88%.

**Bromomethyl(p-chlorophenyl)diphenylsilane (14b).** Obtained from 29b as in Procedure E: white crystals (67%); mp 76-77 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.58-7.35 (m, 14H), 3.16 (s, 2H); MS M* 387.9903 (C\(_{19}\)H\(_{18}\)BrClSi, 0.36%), 293.0648 (C\(_{18}\)H\(_{14}\)ClSi, 100%). Anal. Calcd for C\(_{19}\)H\(_{16}\)BrClSi: C, 58.85%; H, 4.16%. Found. C, 58.78%; H, 4.14%.

**Bromomethyl(triphenylsilane (14c).** Synthesized from 29c as in Procedure E: white crystals (44%); mp 118-120 °C, lit.\(^6\) mp 121-122 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.73-7.36 (m, 14H), 3.20 (s, 2H); MS M* 352.0228 (C\(_{19}\)H\(_{15}\)BrSi, 0.32%), 259.0962 (C\(_{18}\)H\(_{13}\)Si, 100%).

**Bromomethyl(p-methylphenyl)diphenylsilane (14d).** Prepared from 29d as in Procedure E: white crystals (45%); mp 63.5-65.5 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.61-7.35 (m, 12H), 7.35-7.20 (d, 2H), 2.38 (s, 3H), 3.18 (s, 2H); MS M* 366.0467 (C\(_{20}\)H\(_{19}\)BrSi, 0.41%), 273.1112 (C\(_{19}\)H\(_{17}\)Si, 100%). Anal. Calcd for C\(_{20}\)H\(_{19}\)BrSi: C, 65.39%; H, 5.21%. Found: 65.48%; H, 5.27%.

**Bromomethyl(p-methoxyphenyl)diphenylsilane (14e).** Synthesized from 29e as in Procedure E: white crystals (39%); mp 65-66.5 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.60-7.35 (m, 12H), 6.96-6.93 (d, 2H), 3.83 (s, 3H), 3.17 (s, 2H); MS M* 382.0357 (C\(_{20}\)H\(_{19}\)BrOSi, 1.80%), 289.1029 (C\(_{19}\)H\(_{17}\)OSi, 100%). Anal. Calcd for C\(_{20}\)H\(_{19}\)BrOSi: C, 62.66%; H, 5.00%. Found. C, 62.47%; H, 5.03%.

**p-Chlorophenyl(iodomethyl)diphenylsilane (15b).** Prepared from 13b as in Procedure F: white crystals (29%); mp 68-69 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.55-7.35 (m, 14H), 2.70 (s, 2H); MS M* 433.9854 (C\(_{19}\)H\(_{16}\)ClISi, 2.15%), 293.0629 (C\(_{18}\)H\(_{14}\)ClSi, 100%). Anal. Calcd for C\(_{19}\)H\(_{16}\)ClISi: C, 52.49%; H, 3.71%. Found: C, 52.72%; H, 3.74%.

**Iodomethyl(triphenylsilane (15c).** Obtained from 13e as in Procedure F; mp 115-117 °C, lit.\(^26\) mp 117-119 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.62-7.35 (m, 14H), 2.73 (s, 2H); MS M* 400.0150 (C\(_{19}\)H\(_{17}\)ISi, 2.15%), 259.0969 (C\(_{18}\)H\(_{15}\)Si, 100%).

**Iodomethyl(p-methylphenyl)diphenylsilane (15d).** Synthesized from 13d as in Procedure F:
white crystals (49%); mp 75.0-76.5 °C; 1H NMR (CDCl₃) δ 7.61-7.34 (m, 12H), 7.23-7.20 (d, 2H), 2.71 (s, 2H), 2.38 (s, 3H); MS M⁺ 414.0295 (C₂₀H₁₉Si, 2.47%), 273.1180 (C₁₉H₁₇Si, 100%). Anal. Calcd for C₂₀H₁₉Si: C, 57.97%; H, 4.62%. Found: C, 57.87%; H, 4.61%.

(Iodomethyl)(p-methoxyphenyl)diphenylmethane (15e). Synthesized from 13e as in Procedure F: white crystals (39%); mp 59-61 °C; 1H NMR (CDCl₃) δ 7.60-7.27 (m, 12H), 6.96-6.92 (d, 2H), 3.83 (s, 3H), 2.70 (s, 2H); MS M⁺ 430.0228 (C₂₀H₁₉OSi, 2.09%), 289.1068 (C₁₉H₁₇OSi, 71.63%). Anal. Calcd for C₂₀H₁₉OSi: C, 55.82%; H, 4.45%. Found: C, 55.85%; H, 4.47%.

(p-Dimethylaminophenyl)(iodomethyl)diphenylsilane (15f). Prepared from 14f as in Procedure F: white crystals (55%); mp 104-105.5 °C; 1H NMR (CDCl₃) δ 7.62-7.33 (m, 12H), 6.75-6.72 (d, 2H), 2.99 (s, 6H), 2.70 (s, 2H); MS M⁺ 443.0598 (C₂₁H₂₂NSi, 53.00%), 302.1424 (C₂₀H₂₀NSi, 88.19%). Anal. Calcd for C₂₁H₂₂NSi: C, 56.89%; H, 5.02%. Found: C, 56.75%; H, 5.03%.

[(p-Chlorophenyl)methyl]methoxydiphenylsilane (17b, Z-p = Cl). p-Chlorobenzylmagnesium chloride (13 mmol, prepared from p-chlorobenzyl chloride and magnesium) in Et₂O was added (~ 2 h) to a stirred solution of dimethoxydiphenylsilane (62, 2.61 g, 13 mmol) in Et₂O (10 mL). The mixture was refluxed (~ 90 h) until the Grignard reagent was depleted²⁵a. The mixture was cooled and H₂O (15 mL) and then 10% hydrochloric acid (5 mL) were added. Separation, extraction with Et₂O, washing in H₂O and saturated aqueous NaCl, drying over MgSO₄, filtration, and concentration in vacuo yielded an oil which was distilled through a packed column to give 17b, Z-p = Cl (38%): bp 167-172 °C/0.2 torr; 1H NMR δ 7.65-7.10 (m, 10H), 7.00 (d, 2H, J = 8 Hz), 6.75 (d, 2H, J = 8 Hz), 3.45 (s, 3H), 2.50 (s, 2H); MS 338 (M⁺, 2), 214 (20), 213 [M⁺ - (CH₂-C₆H₄Cl), 100], 183 (31), 105 (11); exact mass calcd for C₂₀H₁₉ClOSi m/e 338.0895, found 338.0859.

Methoxy(p-methylphenyl)methylidiphenylsilane (17b, Z-p = CH₃). Prepared from (p-methylphenylmethyl)magnesium chloride and 62²² by the procedure for 17b, Z-p = Cl: 34%, bp
156-160 °C/0.3 torr; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.75-7.15 (m, 10H), 7.85 (bs, 4H), 3.50 (s, 3H), 2.60 (s, 2H), 2.40 (s, 3H); MS 318 (M\(^+\), 5), 214 (20), 2.13 [M\(^+\) - (CH\(_2\)-C\(_6\)H\(_4\)-CH\(_3\)), 100], 183 (27); exact mass calcd for C\(_{21}\)H\(_{22}\)OSi m/e 318.1441, found 318.1464.

\(\textbf{(p-Chlorophenyl)methoxyphenyl(phenylmethyl)silane (20b, Z-p = Cl).}\) \(p\)-Chlorophenyllithium, prepared by addition of n-BuLi (13 mmol) in hexanes (13 mmol) to \(p\)-bromochlorobenzene (13 mmol) in Et\(_2\)O (20 mL) at -40 °C and allowing the mixture to warm to 15 °C until exchange was complete, was added to 63 (3.35 g, 13 mmol) in Et\(_2\)O (10 mL). The mixture was refluxed ~ 90 h and then cooled. Addition of H\(_2\)O and 10% hydrochloric acid, extraction with Et\(_2\)O, drying the extracts, and vacuum-distillation yielded 20b, \(Z-p = Cl\) (22%): bp 178-180 °C/0.5 torr; \(^1\)H NMR \(\delta\) 7.50-6.70 (m, 14H), 3.35 (s, 3H), 2.50 (s, 2H); MS 338 (M\(^+\), 3), 249 (36), 248 (19), 247 (19) [M\(^+\) - (CH\(_2\)-C\(_6\)H\(_4\)), 100], 219 (13), 217 (26); exact mass calcd for C\(_{29}\)H\(_{19}\)Cl\(_4\)Si m/e 338.0895, found 338.0877.

\(\textbf{Methoxydiphenyl(phenylmethyl)silane (20b, Z-p = H).}\) Phenylmagnesium bromide in Et\(_2\)O, prepared from bromobenzene (7.9 g, 50 mmol) and magnesium turnings (1.44 g, 60.0 mmol) in Et\(_2\)O (25 mL), was added (~ 2 h) under argon to 63 (10.0 g, 38.8 mmol) in Et\(_2\)O (10 mL). After reaction was complete (~ 90 h), H\(_2\)O and 10% hydrochloric acid were added. Workup as for 20b, \(Z-p = Cl\) and vacuum distillation yielded 20b, \(Z-p = H\) (3.40 g, 11.2 mmol, 29%) as a clear liquid: bp 175-178 °C/1.5 torr [lit\(^{28}\) 159-161 °C/0.28 torr]; \(^1\)H NMR 7.55-6.80 (m, 15H), 3.45 (s, 3H), 2.60 (s, 2H); MS 304 (M\(^+\), 4), 214 (21), 213 [M\(^+\) - (CH\(_2\)-C\(_6\)H\(_4\)), 100] 183 (32); exact mass calcd for C\(_{20}\)H\(_{20}\)OSi m/e 304.1284, found 304.1283.

\(\textbf{Methoxy(p-methylphenyl)phenyl(phenylmethyl)silane (20b, Z-p = CH\(_3\)).}\) Obtained from reaction of 63 with \(p\)-methylphenyllithium, as generated from n-BuLi and \(p\)-bromotoluene, by the procedure described for 20b, \(Z-p = Cl\), 55%; bp 145-146 °C/0.4 torr; \(^1\)H NMR 7.65-6.85 (m, 14H), 3.50 (s, 3H), 2.65 (s, 2H), 2.40 (s, 3H); MS 318 (M\(^+\), 2), 228 (21), 227 [M\(^+\) - (CH\(_2\)-C\(_6\)H\(_4\)), 100], 197 (27), 193 (11), 137 (13); exact mass calcd for C\(_{21}\)H\(_{22}\)OSi m/e 318.1441, found 318.1477.
**Diphenyl(4-trifluoromethylphenyl)silane (28a).** To a stirred solution of 4-bromo-benzotrifluoride (5.0 g, 0.022 mol) in Et₂O (28 mL) under argon at -40 °C was added n-BuLi (8.9 mL, 2.5 M in hexane, 0.022 mol) in 15 min. The solution was stirred for 10 min, warmed to room temperature, transferred dropwise to dichlorodiphenylsilane (63.9 g, 0.025 mol) in Et₂O, and refluxed for 8 h. The Et₂O was removed by distillation while adding dry benzene until the stillhead temperature reached 78 °C. The reaction mixture was filtered and the benzene removed at reduced pressure to give an orange oil (11.0 g) that was immediately dissolved in dry Et₂O (40 mL) and added at 0 °C to LiAlH₄ (0.60 g, 0.016 mol) in Et₂O (20 mL). The mixture was refluxed overnight. The excess LiAlH₄ was quenched at 0 °C with Et₂O saturated with water and the mixture was then treated with 10% aqueous acetic acid (45 mL). The organic layer was separated and washed with 10% acetic acid (50 mL), water and brine, and dried over Na₂SO₄. The solution was filtered and fractionally distilled to give 28a (5.1 g, 0.016 mol, 70%): bp 145-150 °C, 0.05 torr; ¹H NMR (CDCl₃) 5.50 (s, 1H), 7.3-7.7 (m, 14H).

**(Bromomethyl)chlorodiphenylsilane (30).** Phenylmagnesium bromide (0.52 mol) in Et₂O (500 mL) was added in 2 h to a vigorously stirred solution of bromomethyltrichlorosilane (59.3 g, 0.26 mol) in Et₂O (250 mL). The mixture was refluxed 4 h, cooled to room temperature, filtered under argon, concentrated under reduced pressure, and fractionally distilled to give 30 (13.2 g, 0.042 mol, 17%), bp 136-140 °C (0.5 torr); ¹H NMR (CDCl₃) 3.08 (s, 2H), 7.39-7.77 (m, 10H).