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Preparation of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$ and some related compounds

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Abstract

The preparations of: (a) the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$ (Y = H, *p*-OMe, *p*-Me, *p*-Cl, *m*-CF_3), *via* the corresponding hydrides; (b) the compounds $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2X)$ with X = F, O_2CCF_3, O_2CCH_3, OMe, N_3, NCS and Cl; and (c) the iodide $(p\text{-}MeC_6H_4)_3CSiMe_2I$ are described.

Key words: Silicon; Iodide; Fluoride; Hydride; Trimethylsilyl

1. Introduction

We recently reported the results of mechanistic studies of the reactions of the iodides **1a–1e**, in which the aryl groups can provide powerful anchimeric assistance to the departure of iodide ion [1]. We present below details of the syntheses of these iodides, and of some derivatives **2a–2g** of the phenyl compound. The preparation of the iodide $(p\text{-}MeC_6H_4)_3CSiMe_2I$, containing the new bulky ligand $(p\text{-}MeC_6H_4)_3C$, is also described.

The preparation of the hydroxide (X = OH) has been described previously [1].

$(Me_3Si)_2C(SiMe_2C_6H_4Y)$ $(SiMe_2I)$		$(Me_3Si)_2C(SiMe_2Ph)$ $(SiMe_2X)$	
1a	Y = H	**2a**	X = F
1b	OMe-*p*	**2b**	O_2CCF_3
1c	Me-*p*	**2c**	O_2CCH_3
1d	Cl-*p*	**2d**	OMe
1e	CF_3-*m*	**2e**	Cl
		2f	N_3
		2g	NCS

2. Results and discussion

The first step in the synthesis of each of the iodides **1a–1e** involved the preparation of the fluorides $YC_6H_4Me_2SiF$. These were made by reaction of the Grignard reagent YC_6H_4MgBr with Me_2SiCl_2 to give the chloride $YC_6H_4SiMe_2Cl$, which was then converted into the fluoride, either by treatment with KHF_2 [2] or by hydrolysis to the disiloxane $(YC_6H_4Me_2Si)_2O$ and treatment of the latter, without isolation, with aqueous ethanolic hydrogen fluoride [3].

The next step involved metallation of $(Me_3Si)_2CCl_2$ with ^nBuLi at low temperature to give $(Me_3Si)_2C(Cl)Li$, and treatment of the latter with $YC_6H_4Me_2SiF$ to give $(Me_3Si)_2C(Cl)(SiMe_2C_6H_4Y)$. This was a rather inefficient process, the product after hydrolytic work-up being a mixture of the required $(Me_3Si)_2C(Cl)(SiMe_2C_6H_4Y)$, **C**, along with the compounds $(Me_3Si)_2CH(SiMe_2C_6H_4Y)$, **A**, $(YC_6H_4Me_2Si)_2O$, **B**, and $(Me_3Si)_2C(Bu)(SiMe_2C_6$-$H_4Y)$, **D**. Compound **A** presumably arises by hydrolysis of unused $(Me_3Si)_2C(Li)(SiMe_2C_6H_4Y)$, and compound **D** by reaction of the latter reagent with the BuCl formed in the metallation. (Later experience with related systems suggests to us that formation of species **A** and **D** would be suppressed to some extent by the use of an excess of $YC_6H_4Me_2SiF$.)

For Y = H, the chloride $(Me_3Si)_2C(Cl)(SiMe_2Ph)$ was isolated, in 40% yield, and then treated with ^nBuLi at low temperature followed by Me_2SiHCl, to give the hydride $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2H)$. In the other

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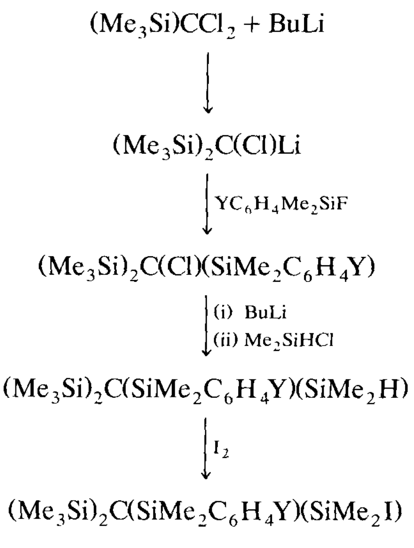
cases, the mixture of products **A**–**D** was treated with BuLi (towards which compounds **A**, **B**, and **D** should be inert) and then with Me_2SiHCl. From the mixture so obtained, the hydride $(Me_3Si)_2C(SiMe_2\text{-}C_6H_4Y)(SiMe_2H)$ was isolated only in the case of Y = *p*-OMe; this hydride, and that with Y = H, were treated with iodine to give the iodides **1b** and **1a** respectively. In other cases the mixtures were treated directly with iodine, and the iodides **1c**, **1d**, and **1e** were allowed to crystallize out during some weeks from the product mixture so obtained. However, the hydride $(Me_3Si)_2C(SiMe_2\text{-}C_6H_4Me\text{-}p)(SiMe_2H)$ was made separately from the mixture left after iodination of the mixture **A**–**D** and removal of the iodide, as described below.

It should be noted that if the iodination of the hydrides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2H)$ is carried out in CCl_4 with iodine alone, there can be extensive cleavage of the Si–aryl bonds by the HI generated, to give the di-iodide $(Me_3Si)_2C(SiMe_2I)_2$, and so the reactions were conducted in the presence of an excess of *p*-$MeOC_6H_4SiMe_3$ (for Y = *p*-OMe), *p*-$MeC_6H_4SiMe_3$ (for Y = Me), or $PhSiMe_3$ (for Y = H, *p*-Cl, and *m*-CF_3, though it may not be necessary in the last two cases because the cleavage would be much slower [4]). Even so, for Y = *p*-OMe, the product solution contained a substantial amount of the diiodide $(Me_3Si)_2C(SiMe_2I)_2$ (as indicated by ^1H NMR spectroscopy), and the proportion of this increased markedly when the mixture was added to aqueous sodium thiosulphate and work-up then carried out in the usual way. Presumably during this treatment, the Me_3SiI also produced in the cleavage is hydrolysed to give more HI, which then rapidly attacks the Si–C_6H_4OMe-*p* bond. The required iodide was ultimately obtained pure only by carrying out the iodination on a small scale in the more volatile solvent CH_2Cl_2, and then rapidly removing the solvent by evaporation under vacuum. The preparation was repeated several times to give an acceptable amount of the required iodide **1b**; attempts to increase the scale always resulted in the formation of a higher proportion of the di-iodide.



Scheme 1.

A further noteworthy point is that for Y = *p*-Cl, after treatment of the mixture of products **A**–**D** with iodine and removal of most of the iodide **1d**, the residual mixture of $(Me_3Si)_2CH(SiMe_2C_6H_4Cl\text{-}p)$, $(p\text{-}ClC_6H_4SiMe_2)_2O$, and $(Me_3Si)_2C(Bu)(SiMe_2C_6H_4Cl\text{-}p)$ and a little of the iodide $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2I)$ was treated with MeLi in boiling THF and with Me_2SiHCl, and from the mixture so obtained the hydride $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2H)$ was isolated by crystallization. The importance of this is that it shows that the compound $(Me_3Si)_2CH(SiMe_2C_6H_4Cl\text{-}p)$ can be metallated normally with MeLi.

The general route to the iodides **1a**–**1e** is shown in Scheme 1.

The compounds $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2X)$ with X = F, $OCOCF_3$, or $OCOCH_3$, were made by treatment of the iodide **1a** with the appropriate silver salts $AgBF_4$, AgO_2CCF_3, and AgO_2CCH_3 respectively. The methoxide **2d** was made by reaction of **1a** with MeOH containing $AgClO_4$ or $HgSO_4$. The chloride **2e** was made by treatment of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2H)$ with a one molar proportion of ICl. (It is difficult to predict with these sterically hindered hydrides whether this treatment will give the chloride or the iodide, though use of an excess of ICl usually ensures formation of the chloride [5].)

The derivatives $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2X)$ with X = N_3 or NCS (**2f** and **2g**) were made by reaction of the iodide **1a** with NaN_3 and KSCN respectively, in MeCN.

2.1. Preparation of $(p\text{-}MeC_6H_4Me_2Si)_3CSiMe_2I$

This novel iodide was made by treatment of $(p\text{-}MeC_6H_4Me_2Si)_3CSiMe_2H$ with iodine. The sample of the latter was made some years ago in this laboratory by Dr. A. Alvanipour, who first made $(p\text{-}MeC_6H_4Me_2Si)_3CH$ from *p*-$MeC_6H_4Me_2SiCl$ by the method used to make $(PhMe_2Si)_3CH$ from $PhMe_2SiCl$ [6], then metallated it with MeLi in refluxing THF as for metallation of $(PhMe_2Si)_3CH$ [7]. Unfortunately the record of the experimental details for his work has been mislaid.

3. Experimental details

3.1. Materials

Solvents, silver salts, and alkali metal salts were carefully dried by standard methods.

3.2. *Spectra*

The ^1H NMR spectra were recorded at 90 MHz on a Perkin Elmer R32 NMR spectrometer or at 360 MHz on a Bruker WM 360 spectrometer. Unless otherwise indicated, solutions were in CCl_4 containing 5 vol.% CH_2Cl_2 as lock and Me_4Si as reference; otherwise they were in $CDCl_3$ as solvent, lock, and reference.

Mass spectra were obtained (by electron impact at 70 eV or, where indicated, by positive chemical ionisation (NH_3)) on a Kratos MS-25 mass spectrometer. For linked GLC-mass spectrometry (GLC-MS) a column of 3% OV-17 on Gas Chrom G (100–200 mesh) was used. (Quantitative significance should not be attached to the relative intensities reported for the various ions observed, and the way in which possible identities of ions are indicated should not be taken as suggesting fragmentation pathways.)

3.3. *Preparation of the fluorides $YC_6H_4SiMe_2F$*

3.3.1. *Y = p-OMe*

The Grignard reagent prepared from p-$MeOC_6H_4Br$ (100 g, 0.53 mol) and magnesium (13.9 g, 0.57 mol) in ether (550 cm^3) was added dropwise during 2 h to a vigorously stirred solution of Me_2SiCl_2 (65 cm^3, 0.54 mol) in ether (200 cm^3). The mixture was stirred for a further 30 min at room temperature, and the ether then removed. The residue was extracted with pentane, the extract filtered, and the solvent taken off under reduced pressure. The residue was added to KHF_2 (excess) [2], the mixture heated gently for 30 min, and the liquid (including some anisole) distilled off. The distillate was redistilled from KF (to remove traces of HF) to yield a mixture of anisole and p-$MeOC_6H_4SiMe_2F$. This mixture was fractionally distilled to give p-$MeOC_6H_4SiMe_2F$ (40 g, 40%), b.p. 218°C. ^1H NMR: δ 0.43 (d, 6H, $SiMe_2F$); 3.76 (s, 3H, OMe); 6.65–7.62 (m, 4H, C_6H_4) ppm. MS m/z: 184 (90%, M); 169 (100, M − Me); 165 (35, $SiMe_2C_6H_4OMe$); 154 (15); 139 (25); 126 (30); 121 (30); 100 (20); 91 (50); 87 (15); 77 (70, $SiMe_2F$); 63 (45); 49 (90).

3.3.2. *Y = p-Me*

The Grignard reagent from p-MeC_6H_4Br (94 g, 0.55 mol) and Mg (13.9 g, 0.57 mol) in ether (165 cm^3) was added dropwise during 1 h to a vigorously stirred solution of Me_2SiCl_2 (50 cm^3, 0.42 mol) in ether (90 cm^3). The mixture was stirred for a further 30 min at room temperature then cooled in an ice-bath and treated with 10% aqueous sulphuric acid until two clear layers had formed. The organic layer was separated, washed well with water, dried ($MgSO_4$), and filtered, and the solvent removed on a rotary evaporator. With precautions appropriate to handling of HF, the residue was added to a mixture of absolute ethanol (220 cm^3) with 40% aqueous HF (80 cm^3) contained in a polyethylene conical flask, and the mixture was kept just below its boiling point for 4.5 h, then added to an excess of water. Ether was added and the organic layer separated, washed with water, dried ($MgSO_4$), and filtered, and the ether was removed on a rotary evaporator. The residue was fractionally distilled to give p-$MeC_6H_4SiMe_2F$ (45 g, 64%), b.p. 183°C. ^1H NMR: δ 0.45 (d, 6H, $SiMe_2F$); 2.36 (s, 3H, Me); 7.16–7.67 (m, 4H, C_6H_4) ppm. MS m/z: 168 (40%, M); 153 (100, M − Me); 148 (15, M − HF); 125 (10); 105 (20); 91 (30); 77 (25); 69 (15); 47 (30); 39 (10).

3.3.3. *Y = H*

This was made from PhBr by the method described under 3.3.2. except that the reaction with the aqueous-alcoholic HF was allowed to proceed for 8 h. The product (65%) had b.p. 162.5°C (lit. [3] 162.4°C). ^1H NMR: δ 0.45 (d, 6H, $SiMe_2$); 7.24–7.71 (m, 5H, Ph) ppm.

3.3.4. *Y = p-Cl*

This was made, from p-ClC_6H_4Br, by the procedure described under 3.3.2. above. The product (62%) had b.p. 199°C. ^1H NMR: δ 0.45 (d, 6H, $SiMe_2F$); 7.27–7.63 (m, 4H, C_6H_4) ppm. MS m/z: 188 (25%, M); 173 (100, M − Me); 125 (5); 97 (5); 91 (10); 77 (5).

3.3.5. *Y = m-CF_3*

This was made, from m-$CF_3C_6H_4Br$, by the procedure described under 3.3.1. above. The product (50%) had b.p. 167–168°C. ^1H NMR: δ 0.49 (d, 6H, $SiMe_2$); 7.40–7.97 (m, 4H, C_6H_4) ppm. MS m/z: 222 (75%, M); 207 (100, M − Me); 203 (20, M − F); 145 (10); 140 (10); 126 (20); 101 (10); 91 (20); 81 (20); 77 (35, M − $C_6H_4CF_3$); 75 (20); 63 (10); 51 (10); 49 (10); 47 (30).

3.4. *Reactions of $(Me_3Si)_2CCl(Li)$ with $YC_6H_4SiMe_2F$*

3.4.1. *Y = Ph*

A 2.5 M solution of BuLi in hexane (29 cm^3, 0.073 mol) cooled to −80°C was added dropwise during 1 h to a stirred solution of $(Me_3Si)_2CCl_2$ (16.6 g, 0.073 mol) in a mixture of THF (160 cm^3), Et_2O (20 cm^3), and n-pentane (8 cm^3) maintained at −110°C. The mixture was stirred at −110°C for a further 2 h then $PhMe_2SiF$ (11.2 g, 0.073 mol) cooled to −78°C was added with stirring. The mixture was kept at −110°C for a further 30 min, allowed to warm to room temperature overnight, and added to saturated aqueous NH_4Cl. The organic layer was separated, washed with water, dried ($MgSO_4$) and filtered, and volatile materials were removed on a rotary evaporator. The residual oil was kept at 100°C/20 mmHg to remove unchanged starting materials and the residue, which solidified on cooling, recrystallized from methanol to give $(Me_3Si)_2C(Cl)(SiMe_2Ph)$ (9.5 g, 40%), with properties identical to those of an authentic sample made in a similar way from $PhMe_2SiCl$ [8].

3.4.2. *Y = p-OMe*

Starting from p-$MeOC_6H_4SiMe_2F$ (0.047 mol) the procedure described under 3.4.1. above was carried out as far as the rotary evaporation and heating of the residue at 100°C/20 mm Hg. The remaining oil was shown by GLC-MS analysis to contain the following four components, A–D, in a 32 : 41 : 21 : 6 ratio.

A. $(Me_3Si)_2CH(SiMe_2C_6H_4OMe$-$p)$. MS *m/z*: 309 (100%. M − Me); 279 (40); 221 (10); 201 (10); 165 (70); 129 (25); 73 (60); 59 (25).

B. $(p$-$MeC_6H_4Si)_2O$. MS *m/z*: 346 (25%, M); 331 (100, M − Me); 316 (10); 299 (30); 269 (30); 223 (20); 209 (20); 165 (45); 135 (15); 121 (20); 105 (10); 91 (25); 73 (30); 59 (20).

C. $(Me_3Si)_2CCl(SiMe_2C_6H_4OMe$-$p)$. MS *m/z*: 343 (15%, M − Me); 323 (5, M − Cl); 235 (15); 165 (100, $SiMe_2C_6H_4OMe$); 85 (25); 73 (95); 59 (50).

D. $(Me_3Si)_2C(Bu)(SiMe_2C_6H_4OMe$-$p)$. MS *m/z*: 380 (5%, M); 365 (10, M − Me); 200 (10); 185 (20); 165 (100, $SiMe_2C_6H_4OMe$); 126 (10); 83 (5); 73 (65); 59 (15).

3.4.3. *Y = p-Me*

Starting from p-$MeC_6H_4SiMe_2F$ (0.089 mol) the procedure described under 3.4.2. above gave a mixture of four products, A–D, in 26 : 37 : 35 : 2 ratio as follows.

A. $(Me_3Si)_2CH(SiMe_2C_6H_4Me$-$p)$. MS *m/z*: 293 (100%, M − Me); 149 (25); 129 (15); 73 (35); 59 (10).

B. $(p$-$MeC_6H_4SiMe_2)_2O$. MS *m/z*: 314 (20%, M); 299 (100, M − Me); 207 (60); 193 (10); 149 (15).

C. $(Me_3Si)_2C(Cl)(SiMe_2C_6H_4Me$-$p)$. MS *m/z*: 327 (5%, M − Me); 234 (10, M − Me_3SiCl); 219 (10); 149 (100, $SiMe_2C_6H_4Me$); 73 (40); 59 (10).

D $(Me_3Si)_2C(Bu)(SiMe_2C_6H_4Me$-$p)$. MS *m/z*: 349 (5%, M − Me); 200 (35), M − $Me_3SiC_6H_4Me$); 185 (30); 149 (100); 126 (15); 73 (75); 59 (15).

3.4.4. *Y = p-Cl*

Starting from p-$ClC_6H_4SiMe_2F$ (0.068 mol) the procedure described under 3.4.2. above gave a mixture of four products, A–D, in 27 : 28 : 16 : 29 ratio as follows.

A. $(Me_3Si)_2CH(SiMe_2C_6H_4Cl$-$p)$. MS *m/z*: 313 (50%, M − Me); 205 (10); 169 (20); 129 (65); 73 (100, Me_3Si^+); 59 (25).

B. $(p$-$ClC_6H_4SiMe_2)_2O$. MS *m/z*: 354 (5%, M); 339 (80, M − Me); 303 (100, M − Me − HCl); 267 (55); 229 (75); 165 (45); 91 (75); 73 (55).

C. $(Me_3Si)_2C(Cl)(SiMe_2C_6H_4Cl$-$p)$. MS *m/z*: 347 (5%, M − Me); 311 (10); 274 (10); 239 (25); 169 (75); 135 (12); 93 (15); 73 (100); 59 (20).

D. $(Me_3Si)_2C(Bu)(SiMe_2C_6H_4Cl$-$p)$. MS *m/z*: 369 (5%, M − Me); 200 (20).

3.4.5. *Y = m-CF₃*

Starting from m-$CF_3C_6H_4SiMe_2F$ (0.033 mol) the procedure described under 3.4.2. above gave four products, A–D, in 34 : 34 : 25 : 7 ratio, as follows.

A. $(Me_3Si)_2CH(SiMe_2C_6H_4CF_3$-$m)$. MS *m/z*: 347 (95%, M − Me); 203 (215); 181 (5); 129 (20); 73 (100); 59 (30).

B. $(m$-$CF_3C_6H_4SiMe_2)_2O$. MS *m/z*: 407 (100%, M − Me); 347 (35); 281 (10); 203 (35); 155 (20); 129 (10); 91 (15); 73 (50); 59 (10).

C. $(Me_3Si)_2C(Cl)(SiMe_2C_6H_4CF_3$-$m)$. MS *m/z*: 361 (15%, M − Cl); 203 (20); 143 (10); 73 (100); 59 (20).

D. $(Me_3Si)_2C(Bu)(SiMe_2C_6H_4CF_3$-$m)$. MS *m/z*: 403 (70%, M − Me); 209 (20); 203 (15); 129 (15); 73 (100); 59 (15).

3.5. *Preparation of the hydrides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2H)$*

3.5.1. *Y = p-OMe*

The 32 : 41 : 21 : 6 mixture (9.85 g) of $(Me_3Si)_2CH(SiMe_2C_6H_4OMe$-$p)$, $(Me_3Si)_2C(Cl)(SiMe_2C_6H_4OMe$-$p)$, $(p$-$MeOC_6H_4SiMe_2)_2O$, and $(Me_3Si)_2C(Bu)(SiMe_2C_6H_4OMe$-$p)$ obtained as described above was dissolved in a mixture of THF (200 cm^3), Et_2O (10 cm^3) and pentane (10 cm^3) and the solution was maintained at −100°C as a 2.6 M solution of BuLi in hexane (20 cm^3, 0.052 mol), cooled to −80°C, was added dropwise. After a further 2 h stirring at −110°C, Me_2SiHCl (6.5 cm^3, 0.059 mol) cooled to −80°C was added dropwise with stirring. The mixture was allowed to warm to room temperature overnight. Volatile materials were removed under reduced pressure, the residue extracted with pentane, and the extract filtered and evaporated to dryness. The residual oil was dissolved in Et_2O, MeOH was added, and the solution kept at −20°C overnight. The white solid was filtered off and recrystallized from MeOH to give crystalline $(Me_3Si)_2C(SiMe_2C_6H_4OMe$-$p)(SiMe_2H)$ (4.1 g), m.p. 78.6°C. Anal. Found: C, 56.6; H, 9.7. $C_{18}H_{38}OSi_4$ calc.: C, 56.5; H, 9.95%. ^1H NMR ($CDCl_3$): δ 0.13 (d, 6H, $J = 3.73$ Hz, Si*Me*$_2$H); 0.15 (s, 18H, $SiMe_3$); 0.48 (s, 6H, Si*Me*$_2$aryl); 3.79 (s, 3H, OMe); 4.41 (m, 1H, SiH); 6.82–7.63 (m, 4H, C_6H_4) ppm. MS *m/z*: 382 (15%, M); 367 (55, M − Me); 365 (70, M − Me − MeH); 274 (95, M − C_6H_4OMe); 216 (15); 201 (95); 165 (100, $SiMe_2C_6H_4OMe$); 129 (30).

3.5.2. $Y = p$-Me

(i) (With conversion of the hydride without isolation, into the iodide.)

As described for $Y = p$-OMe above, the 26:37:35:2 mixture (16.0 g) of $(Me_3Si)_2CH(SiMe_2C_6H_4Me\text{-}p)$, $(p\text{-}MeC_6H_4SiMe_2)_2O$, $(Me_3Si)_2C(Cl)(SiMe_2C_6H_4Me\text{-}p)$ and $(Me_3Si)_2C(Bu)(SiMe_2C_6H_4Me\text{-}p)$ was treated with BuLi and then with Me_2SiHCl. Work-up as in 3.5.1. was follows as far as the evaporation of the extract to leave an oil (12 g). This oil (which was shown by ^1H NMR spectroscopy to contain $(Me_3Si)_2C(SiMe_2C_6H_4\text{-}Me\text{-}p)(SiMe_2H)$) was dissolved in CCl_4 (240 cm^3), and p-$MeC_6H_4SiMe_3$ (4.5 g, 0.03 mol) was added, followed by a solution of I_2 (8.4 g, 0.03 mol) in CCl_4 (160 cm^3). The mixture was stirred at room temperature for 3 h then residual I_2 was destroyed by shaking with aqueous $Na_2S_2O_7$. The organic layer was separated, washed, dried ($MgSO_4$) and filtered, and solvent was removed under reduced pressure. The residue was set aside in an open vessel, and after some weeks the formed crystals were separated and recrystallized from MeOH to give pure $(Me_3Si)_2C(SiMe_2C_6H_4Me\text{-}p)(SiMe_2I)$ (2.0 g) with properties identical to those of the material obtained by an alternative method (see later).

(ii) A 2.6 M solution of BuLi in hexane (34 cm^3, 0.088 mol) cooled to −80°C was added during 1 h to a stirred solution of $(Me_3Si)_2CCl_2$ (9.8 g, 0.043 mol) in a mixture of THF (80 cm^3), Et_2O (10 cm^3), and pentane (4 cm^3) maintained at −110°C. The mixture was stirred for a further 2 h at −110°C then p-$MeC_6H_4SiMe_2F$ (7.35 g, 0.044 mol), cooled to −80°C, was added dropwise with stirring. This mixture was allowed to warm to room temperature overnight, and the solvents and residual Me_2SiHCl were then removed on a rotary evaporator. Unchanged starting materials and some higher-boiling products were distilled off at 100°C/0.3 mmHg, and the residue, which solidified on cooling, was extracted with pentane, the extract was filtered and evaporated, and the residue recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2C_6H_4Me\text{-}p)(SiMe_2H)$ (5.4 g, 34%), m.p. 83°C. Anal. Found: C, 59.8; H, 9.6. $C_{18}H_{38}Si_4$ calc.: C, 59.0, H, 10.4%. ^1H NMR ($CDCl_3$): δ 0.15 (d, 6H, $J = 3.72$ Hz, $SiMe_2H$); 0.16 (s, 18H, $SiMe_3$); 0.30 (s, 6H, $SiMe_2$aryl); 2.33 (s, 3H, p-Me); 4.44 (m, 1H, SiH); 7.08–7.61 (m, 4H, C_6H_4) ppm. MS m/z: 336 (10%, M); 351 (30, M − Me); 349 (55); 293 (20, M-$SiMe_3$); 274 (50, M − C_6H_4Me); 201 (40); 187 (15); 149 (75); 129 (20); 73 (100); 59 (15).

3.5.3. $Y = H$

A 2.5 M solution of BuLi in hexane (100 cm^3, 0.25 mol), cooled to −80°C, was added dropwise to a stirred solution of $(Me_3Si)_2C(Cl)(SiMe_2Ph)$ (15.5 g, 0.047 mol) in a mixture of THF (160 cm^3), Et_2O (20 cm^3), and pentane (8 cm^3) maintained at −110°C. The mixture was stirred at −110°C) for a further 2 h then allowed to warm to −78°C and Me_2SiHCl (32 cm^3, 0.29 mol), cooled to −78°C, was added dropwise with stirring. The mixture was stirred at −78°C for a further 0.5 h then allowed to warm to room temperature. Volatile materials were removed under reduced pressure and the residual solid extracted with pentane. The extract was filtered and evaporated, and the residue recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2\text{-}H)$ (11.3 g, 68%), m.p. 83°C. Anal. Found: C, 58.1; H, 10.5. $C_{17}H_{36}Si_4$ calc.: C, 58.0; H, 10.2%. ^1H NMR ($CDCl_3$): δ 0.15 (d, 6H, $J = 3.74$ Hz, $SiMe_2H$); 0.17 (s, 18H, $SiMe_3$); 0.52 (s, 6H, $SiMe_2Ph$); 4.47 (s, 1H, SiH); 7.26–7.73 (m, 5H, Ph) ppm. MS m/z: 352 (5%, M); 337 (35, M − Me); 274 (10); 247 (20); 216 (10); 201 (25); 187 (5); 175 (20); 135 (45); 129 (15); 73 (100); 59 (15). The properties are in satisfactory agreement with those reported previously [8].

3.5.4. $Y = p$-Cl (with conversion into the iodide)

The 27:28:16:29 mixture (12.9 g) of $(Me_3Si)_2CH\text{-}(SiMe_2C_6H_4Cl\text{-}p)$, $(p\text{-}ClC_6H_4SiMe_2)_2O$, $(Me_3Si)_2C\text{-}(Cl)(SiMe_2C_6H_4Cl\text{-}p)$, and $(Me_3Si)_2C(Bu)(SiMe_2\text{-}C_6H_4Cl\text{-}p)$ was treated with BuLi (0.070 mol) and then with Me_2SiHCl as described for the compound with $Y = p$-OMe in 3.5.1. above. Work-up, as in the latter case, gave an oil that was shown from its ^1H NMR spectrum to contain $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)\text{-}(SiMe_2H)$, along with three inert components of the initial mixture. The product mixture (13.1 g) was dissolved in CCl_4 (80 cm^3) containing Me_3SiPh (5.2 g, 0.035 mol) and a solution of I_2 (7.8 g, 0.31 mol) in CCl_4 (50 cm^3) was added. The mixture was stirred at room temperature for 3 h, then the residual iodine was destroyed by shaking with aqueous $Na_2S_2O_7$. The organic layer was separated, washed with water, dried ($MgSO_4$) and filtered, and solvents taken off under pressure. The remaining oil was set aside in an open vessel for some weeks, and the crystals that separated were collected, and recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2I)$ (1.30 g), m.p. 169°C. ^1H NMR: δ 0.34 (s, 18H, $SiMe_3$); 0.68 (s, 6H, $SiMe_2$aryl); 1.02 (s, 6H, $SiMe_2I$); 7.22–7.87 (m, 4H, C_6H_4) ppm. MS m/z: 497 (5%, M − Me); 385 (75, M − I); 369 (30); 349 (10); 297 (10); 281 (15); 221 (10); 201 (45); 185 (15); 169 (30); 127 (10); 73 (100); 59 (15).

The remaining oil, after the removal of the crystals of the iodide, was dissolved in THF (100 cm^3), a 1.0 M solution of MeLi (46 cm^3, 0.046 mol) was added, the mixture was refluxed for 8 h, Me_2SiHCl (15 cm^3, 0.14 mol) was added. The mixture was stirred overnight at room temperature and then added cautiously to an excess of saturated aqueous NH_4Cl. The organic layer was separated, washed with water, dried ($MgSO_4$), and filtered, and volatile materials were removed on a rotary evaporator under reduced pressure. The residual oil was dissolved in a minimum of Et_2O, MeOH was added, and the solution kept overnight at −20°C. The white solid that formed was filtered off and recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2C_6H_4Cl$-*p*$)(SiMe_2H)$ containing a small amount of the corresponding iodide. Sublimation (120°C/2 mmHg) left behind the iodide to give pure $(Me_3Si)_2C(SiMe_2C_6H_4$-Cl-*p*$)(SiMe_2H)$ (1.9 g), m.p. 106°C. Anal. Found: C, 52.8; H, 9.3. $C_{17}H_{35}ClSi_4$ calc.: C, 52.7; H, 9.1%. ^1H NMR ($CDCl_3$): δ 0.14 (d, 6H, $J = 3.87$ Hz, $SiMe_2H$); 0.15 (s, 18H, $SiMe_3$); 0.48 (s, 6H, $SiMe_2$aryl); 4.41 (m, 1H, SiH); 7.24–7.64 (m, 4H, C_6H_4) ppm. MS *m/z*: 371 (35%, M − Me); 369 (35); 274 (25, $M - C_6H_5Cl$); 201 (25); 169 (21, $SiMe_2C_6H_4Cl$); 129 (15); 73 (100); 59 (15).

3.5.5. *Y = m-CF₃ (with conversion into the iodide $(Me_3Si)_2C(SiMe_2C_6H_4CF_3$-m$)(SiMe_2I)$)*

The 34:34:25:7 mixture (4.7 g) of $(Me_3Si)_2CH(SiMe_2C_6H_4CF_3$-*m*$)$, $(m\text{-}CF_3C_6H_4SiMe_2)_2O$, $(Me_3Si)_2C(Cl)(SiMe_2C_6H_4CF_3$-*m*$)$, and $(Me_3Si)_2C(Bu)(SiMe_2C_6H_4CF_3$-*m*$)$ obtained as described above was treated with BuLi (0.026 mol) followed by Me_2SiHCl (0.027 mol) as described for the compound with Y = *p*-OMe under 3.5.1. above. After the usual hydrolytic work-up the obtained oil was shown by ^1H NMR spectroscopy to contain $(Me_3Si)_2C(SiMe_2C_6H_4CF_3$-*m*$)(SiMe_2H)$. ^1H NMR ($CDCl_3$): δ 0.20 (d, 6H, $J = 3.74$ Hz, $SiMe_2H$); 0.19 (s, 18H, $SiMe_3$); 0.57 (s, 6H, $SiMe_2$aryl); 4.48 (m, 1H, $J = 3.72$ Hz, SiH); 7.39–8.00 (m, 4H, C_6H_4) ppm; along with the three inert components of the original oil. The product mixture was dissolved in CCl_4 (60 cm^3) containing Me_3SiPh (1.2 cm^3, 7 mmol); iodine (1.89 g, 7.4 mmol) was added, and the mixture was stirred at room temperature overnight. The remaining I_2 was removed by shaking the solution with aqueous $Na_2S_2O_7$, and the organic layer was separated, washed with water, dried ($MgSO_4$), and filtered, and the solvent removed under reduced pressure. The obtained oil was set aside in an open vessel for some weeks, and the crystals that had been formed were then collected and recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2C_6H_4CF_3$-*m*$)(SiMe_2I)$ (0.5 g), m.p. 61°C. ^1H NMR: δ 0.34 (s, 18H, $SiMe_3$); 0.73 (s, 6H, $SiMe_2$aryl); 1.01 (s, 6H, $SiMe_2I$); 7.17–8.17 (m, 4H, C_6H_4) ppm. MS *m/z*: 531 (10%, M − Me); 419 (100, M − I); 203 (40, $SiMe_2C_6H_4CF_3$); 159 (10); 127 (10); 77 (30); 60 (20). MS *m/z* (+CI/NH_3): 564 (10%, $M + NH_4$); 419 (100, M − I).

3.6. *Preparation of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$*

3.6.1. *Y = H*

A solution of I_2 (2.17 g, 8.54 mmol) in CCl_4 (25 cm^3) was added to one of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2H)$ (1.50 g, 4.26 mmol) in CCl_4 (25 cm^3) containing Me_3SiPh (1.3 g, 8.6 mmol). The solution was stirred for 4 h at room temperature, then shaken with an excess of aqueous $Na_2S_2O_7$ to remove the remaining iodine, dried ($MgSO_4$), filtered, and evaporated. The residual white solid was recrystallized from n-pentane to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$ (1.60 g, 79%), m.p. 217°C. Anal. Found: C, 42.2; H, 7.4%. $C_{17}H_{35}ISi_4$ calc.: C, 42.65; H, 7.4%. ^1H NMR: δ 0.35 (s, 18H, $SiMe_3$); 0.69 (s, 6H, $SiMe_2Ph$); 1.02 (s, 6H, $SiMe_2I$); 7.20–7.93 (m, 5H, Ph) ppm. MS *m/z*: 463 (5%, M − Me); 371 (10, M − Me − PhMe); 351 (70, M − I); 335 (60, M − Me − HI); 247 (25); 201 (45); 175 (20); 135 (55, $SiMe_2Ph$); 73 (100); 59 (10).

3.6.2. *Y = p-Me*

The procedure described immediately above for the phenyl analogue, but starting from $(Me_3Si)_2C(SiMe_2C_6H_4Me$-*p*$)(SiMe_2H)$ (2.9 mmol) and iodine (5.8 mmol) in the presence of *p*-$MeC_6H_4SiMe_3$ (11.5 mmol) gave $(Me_3Si)_2C(SiMe_2C_6H_4Me$-*p*$)(SiMe_2I)$ (86%), m.p. 152°C. Anal. Found: C, 43.0; H, 7.4. $C_{18}H_{37}ISi_4$ calc.: C, 43.9; H, 7.6%. ^1H NMR: δ 0.34 (s, 18H, $SiMe_3$); 0.66 (s, 6H, $SiMe_2$aryl); 1.02 (s, 6H, $SiMe_2I$); 2.33 (s, 3H, *p*-Me); 7.02–7.74 (m, 4H, C_6H_4) ppm. MS *m/z*: 401 (5%, $M - C_6H_4Me$); 365 (70, M − I); 349 (45, M − Me − HI); 335 (10); 261 (15); 201 (30); 149 (45); 73 (100); 59 (25).

3.6.3. *Y = p-OMe*

A solution of iodine (0.29 g, 1.14 mmol) in CH_2Cl_2 (2 cm^3) was added to a stirred solution of $(Me_3Si)_2C(SiMe_2C_6H_4OMe$-*p*$)(SiMe_2H)$ (0.22 g, 0.58 mmol) and *p*-$MeOC_6H_4SiMe_3$ (0.40 g, 2.22 mmol) in CH_2Cl_2 (1 cm^3). The mixture was stirred for a further 30 min at room temperature then evaporated to dryness under vacuum. The residue was dissolved in CCl_4, and the CCl_4 was then removed under vacuum, taking some of the residual iodine with it; this procedure was repeated until the residue was white. The whole of the above procedure was repeated twice, and the three samples of solid obtained were combined. Some $(Me_3Si)_2C(SiMe_2I)_2$ present was sublimed out at 100°C/0.2 mmHg, and the residue recrystallized from pentane (at this stage a little of the di-iodide $(Me_3Si)_2C(SiMe_2I)_2$ was present), and finally sublimed at 120°C/0.2 mmHg to give pure $(Me_3Si)_2C(SiMe_2C_6H_4OMe$-*p*$)(SiMe_2I)$ (0.54 g, 62%), m.p. 159°C. Anal. Found: C, 41.9; H, 7.0.

$C_{18}H_{37}IOSi_4$ calc.: C, 42.5; H 7.3%. ^1H NMR: δ 0.34 (s, 18H, $SiMe_3$); 0.65 (s, 6H, Si*Me*$_2$aryl); 1.01 (s, 6H, $SiMe_2I$); 3.78 (s, 3H, OMe); 6.79–7.90 (m, 4H, C_6H_4) ppm. MS *m/z*: 493 (5%, M − Me); 381 (100, M − I); 277 (10); 201 (25); 165 (40, $SiMe_2C_6H_4OMe$); 73 (55).

[As noted in the Results and discussion section, when the above reaction was carried out with larger quantities of the reagents the exclusive or predominant product was the di-iodide $(Me_3Si)_2C(SiMe_2I)_2$.]

3.7. Preparation of the compounds $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2X)$ (X = Cl, F, O_2CCF_3, O_2CCH_3, OMe, N_3, or NCS)

3.7.1. X = Cl

(i) A solution of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2H)$ (0.034 g, 0.097 mmol) in 0.10 M ICl in CCl_4 (1.0 cm^3, 0.10 mmol) was stirred at room temperature for 10 min then evaporated to dryness. The residue was taken up in CCl_4 and the latter then removed under reduced pressure. This procedure was repeated until the iodine colour had disappeared from the solid. The solid was then sublimed at 110°C/0.2 mmHg to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2Cl)$ (0.028 g, 75%), m.p. 192°C. Anal. Found: C, 51.8; H, 9.1. $C_{17}H_{35}Si_4Cl$ calc.: C, 52.7, H, 9.1%. ^1H NMR ($CDCl_3$): δ 0.28 (s, 18H, $SiMe_3$); 0.49 (s, 6H, $SiMe_2Cl$); 0.62 (s, 6H, Si*Me*$_2$Ph); 7.24–8.08 (m, 5H, Ph) ppm. MS *m/z*: 371 (35%, M − Me); 335 (45, M − Me − HCl); 263 (10); 247 (10); 216 (20); 201 (30); 175 (21); 135 (45); 73 (100); 59 (20).

(ii) A solution of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$ (0.048 g, 0.10 mol) in 0.10 M ICl in CCl_4 (1.0 cm^3, 0.10 mmol) was stirred at room temperature for 25 min. Work-up as in (i) above, culminating in sublimation, gave the same product (0.031 g, 80%), with properties identical to those listed above.

3.7.2. X = F

A mixture of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$ (0.081 g, 0.17 mmol) and $AgBF_4$ (0.036 g, 0.18 mmol) in Et_2O (5 cm^3) was stirred at room temperature overnight. The solvent was removed under reduced pressure and the solid residue extracted with pentane. The extract was filtered and evaporated to dryness and the residue recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2F)$ (0.053 g, 85%), m.p. 89°C. Anal. Found: C, 56.0; H, 9.9 $C_{17}H_{35}Si_4F$ calc.: C, 55.1; H, 9.5%. ^1H NMR ($CDCl_3$): δ 0.21 (s, 18H, $SiMe_3$); 0.22 (d, 6H, J = 7.57 Hz, $SiMe_2F$); 0.55 (d, 6H, J = 0.49 Hz, Si*Me*$_2$Ph); 7.24–7.92 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$, with $CFCl_3$ as reference): δ −139.95 (m, J(HF) = 7.72 Hz) ppm. MS *m/z*: 355 (85, M − Me); 263 (35, M − Me − Me_3SiF); 247 (20); 201 (90); 175 (55); 139 (95); 73 (100); 59 (55). MS *m/z* (+ve CI/NH_3): 388 (5%, M + NH_4); 355 (100, M − Me).

3.7.3. X = O_2CCF_3

(i) A mixture of **1a** (0.045 g, 0.094 mmol) and AgO_2CCF_3 (0.12 g, 0.54 mmol) in CH_2Cl_2 (5 cm^3) was stirred under reflux for 2 h. The solvent was removed under reduced pressure, the residue extracted with pentane, the extract filtered and evaporated, and the residue recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2O_2CCF_3)$ (0.035 g, 80%), m.p. 64°C. Anal. Found: C, 49.3; H, 7.5. $C_{19}H_{35}F_3O_2Si_4$ calc.: C, 49.1; H, 7.6%. ^1H NMR: δ 0.31 (s, 18H, $SiMe_3$); 0.41 (s, 6H, $SiMe_2O$); 0.63 (s, 6H, Si*Me*$_2$Ph); 7.26–7.92 (m, 5H, Ph) ppm. MS *m/z*: 464 (5%, M); 449 (70, M − Me); 399 (75); 351 (55); 299 (50); 297 (75); 275 (50); 247 (30); 205 (85); 175 (75) 135 (95); 105 (100); 77 (85). MS *m/z* (+ve CI/NH_3): 482 (5%, M + NH_4); 105 (100).

(ii) Trifluoroacetic acid (5 cm^3) was added to a mixture of $(Me_3Si)_2C(SiMe_2I)(SiMe_2Ph)$ (0.26 g, 0.54 mmol) and Ag_2O (0.37 g, 1.59 mmol). The ^1H NMR spectrum, recorded as quickly as possible (< 2 min), showed that only $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2O_2CCF_3)$ was present. The solution was added to ice-water, and the organic material extracted with pentane. The extract was filtered and evaporated to dryness and the residue recrystallized from MeOH to give $(Me_3Si)_2C$ $(SiMe_2Ph)(SiMe_2O_2CCF_3)$ (0.21 g, 83%), with properties identical to those listed above.

3.7.4. X = O_2CCH_3

(i) A mixture of **1a** (0.046 g, 0.096 mmol) and AgO_2CCH_3 (0.021 g, 0.13 mmol) in CH_2Cl_2 was stirred under reflux for 3 h. The solvent was removed under reduced pressure and the residue extracted with pentane. The extract was filtered and evaporated to dryness and the residue recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2O_2CCH_3)$ (0.32 g, 81%), m.p. 89°C. Anal. Found: C, 55.5, H, 9.6. $C_{19}H_{38}O_2Si_4$ calc.: C, 55.6; H, 9.3%. ^1H NMR ($CDCl_3$): δ 0.25 (s, 18H, $SiMe_3$); 0.35 (s, 6H, $SiMe_2O$); 0.58 (s, 6H, Si*Me*$_2$Ph); 2.12 (s, 3H, O_2CCH_3); 7.24–7.83 (m, 5H, Ph) ppm. MS *m/z*: 395 (50%, M − Me); 353 (25); 337 (45, M − $SiMe_3$); 323 (10); 275 (85); 263 (10); 247 (20); 201 (35); 187 (70); 175 (35); 147 (15); 135 (90); 117 (35); $SiMe_2O_2CCH_3$); 73 (100); 59 (25).

(ii) A mixture of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OH)$ [1] (0.076, 0.21 mmol), CH_3COCl (5 cm^3), and Me_3SiPh (2.0 cm^3) was left overnight at 60°C then evaporated to dryness under reduced pressure. The residue was sublimed at 110°C/0.2 mmHg to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2O_2CCH_3)$ (0.056 g, 66%) with properties identical to those listed above.

3.7.5. X = OMe

(i) A stirred mixture of **1a** (0.082 g, 0.17 mmol) and $AgClO_4$ (0.107 g, 0.52 mmol) in MeOH was refluxed under N_2 for 0.5 h. (The reaction would probably have been complete in a much shorter time even at room temperature.) The solvent was removed under reduced pressure and the residue sublimed (100°C/0.2 mmHg) to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OMe)$, m.p. 177°C. Anal. Found: C, 56.0; H, 9.7. $C_{18}H_{38}OSi_4$ calc.: C, 56.5; H, 9.95%. ^1H NMR ($CDCl_3$): δ 0.09 (s, 6H, Si*Me*$_2$OMe); 0.19 (s, 18H, $SiMe_3$); 0.52 (s, 6H, Si*Me*$_2$Ph); 3.39 (s, 3H, OMe); 7.13–7.84 (m, 5H, Ph) ppm. MS *m/z*: 367 (30%, M – Me – MeOH); 351 (10); 335 (30); 305 (10); 279 (15); 275 (10); 263 (10); 247 (25); 217 (30); 201 (20); 187 (20); 175 (25); 135 (50); 129 (15); 121 (10); 105 (10); 89 (15); 73 (100); 59 (30).

(ii) A mixture of **1a** (0.085 g, 0.178 mmol) and $HgSO_4$ (0.25 g, 0.084 mmol) in MeOH (10 cm^3) was refluxed for 1 h, and the solvent then removed under reduced pressure. The residue was extracted with pentane and the extract was filtered and evaporated to dryness. The residue was sublimed (100°C/0.2 mmHg) to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OMe)$ (0.053 g, 78%), with properties identical to those listed above.

3.7.6. Y = N_3

A sample of **1a** (0.064 g, 0.13 mmol) was dissolved in a minimum amount of CCl_4, anhydrous MeCN (10 cm^3) was added, and the solution refluxed with NaN_3 (0.10 g, 1.54 mmol) for 24 h. The solvent was then removed under vacuum, and the residue extracted with pentane, the extract filtered, and evaporated to dryness. The residue was sublimed (110°C/0.2 mmHg) to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2N_3)$ (0.042 g, 80%), m.p. 125°C. ^1H NMR: δ 0.26 (s, 18H, $SiMe_3$); 0.32 (s, 6H, $SiMe_2N_3$); 0.59 (s, 6H, Si*Me*$_2$Ph); 7.19–7.94 (m, 5H, Ph) ppm. MS *m/z*: 378 (5%, M – Me); 350 (25); 277 (10); 262 (20); 200 (20); 135 (60); 116 (10); 100 (10); 73 (100); 59 (10).

3.7.7. Y = NCS

A sample of **1a** (0.037 g, 7.74 mmol) was dissolved in a minimum amount of CCl_4 and a 0.25 M solution of KSCN in anhydrous MeCN (1.0 cm^3) was added. The solution was kept at 60°C for 3 h, the solvent removed under vacuum, the residue extracted with pentane, and the extract filtered and evaporated. The solid was sublimed (110°C/0.2 mmHg) to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2NCS)$ (0.025 g, 79%), m.p. 118°C. Anal. Found: C, 52.2; H, 8.5; N, 3.1. $C_{18}H_{35}NSSi_4$ calc.: 52.75; H, 8.6; N, 3.4%. ^1H NMR: δ 0.30 (s, 18H, $SiMe_3$); 0.32 (s, 6H, $SiMe_2NCS$); 0.62 (s, 6H, Si*Me*$_2$Ph); 7.20–7.86 (m, 5H, Ph) ppm. MS *m/z*: 409 (10%, M); 394 (100, M – Me); 335 (85); 259 (15); 247 (15); 201 (20); 175 (15); 135 (50); 73 (60).

3.8. Preparation of $(p\text{-}MeC_6H_4Me_2Si)_3CSiMe_2I$

A solution of iodine (0.69 g, 2.72 mmol) in CCl_4 (20 cm^3) was added to a stirred solution of $(p\text{-}MeC_6H_4Me_2Si)_3CSiMe_2H$ (0.70 g, 1.35 mmol) in CCl_4 (20 cm^3) containing $p\text{-}MeC_6H_4SiMe_3$ (1.08 g, 6.58 mmol). The mixture was stirred at room temperature for 3 h then shaken with aqueous sodium thiosulphate to remove residual iodine. The organic layer was separated, washed, dried ($MgSO_4$), filtered, and evaporated under vacuum to leave a white solid which was recrystallized from hexane to give $(p\text{-}MeC_6H_4Me_2Si)_3CSiMe_2I$ (0.63 g, 72%), m.p. 186°C. ^1H NMR: δ 0.70 (s, 18H, Si*Me*$_2$aryl); 1.15 (s, 6H, $SiMe_2I$); 2.33 (s, 9H, *p*-Me); 6.57–6.97 (m, 12H, C_6H_4) ppm. MS *m/z*: 517 (10%, M – I); 425 (95, M – I – PhMe); 409 (40); 337 (25); 261 (30); 225 (25); 189 (30); 149 (100, $MeC_6H_4Me_2Si$); 119 (20); 91 (65); 73 (60).

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