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Organophosphorus and organosilicon derivatives of sterically hindered phenols

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Abstract

A general methodology for the preparation of sterically hindered hydroxyaryl derivatives of both phosphorus and silicon is described. The reaction of 3,5-di-t-butyl-4-trimethylsilyloxyphenyllithium (**4**), which was prepared by the metalation of 1-bromo-3,5-di-t-butyl-4-trimethylsilyloxybenzene with n-butyllithium at −78 °C, with chlorodiphenylphosphine gave the protected phenolic derivative 3,5-di-t-butyl-4-trimethylsilyloxyphenyl(diphenyl)phosphine (**5**). Similarly, the reaction of **4** with dichlorophenylphosphine and phosphorus trichloride afforded the bis- and tris-adducts, bis(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)phenylphosphine (**7a**) and tris(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)phosphine (**7b**), respectively. Aqueous hydrolysis of **5** and **7a**, **7b** gave the corresponding 3,5-di-t-butyl-4-hydroxyphenylphosphines **1b** and **8a**, **8b**, respectively. The reaction of **4** with the dimethyl-, diphenyl-, and methyl-substituted dichlorosilanes **9a–c** gave the corresponding bis(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)silanes **10a–10c**. Removal of the trimethylsilyl protecting group with *N,N,N,N*-tetra-n-butylammonium fluoride trihydrate (TBAF, trihydrate) gave the corresponding bis(3,5-di-t-butyl-4-hydroxyphenyl)silanes **11a–11c**, respectively. In the case of **10c**, besides the expected derivative **11c**, the fluoro-substituted silane bis(3,5-di-t-butyl-4-hydroxyphenyl)methylfluorosilane (**12**) was isolated. A plausible mechanism for the formation of **12** involving a pentacoordinate siliconate anion intermediate or transition state **13** was suggested. The reaction of **4** with silicon(IV) chloride followed by aqueous hydrolysis gave the trisubstitution product tris(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)silanol (**14**). Deprotection of **14** with TBAF · trihydrate gave the trisadduct tris(3,5-di-t-butyl-4-hydroxyphenyl)silanol (**15**).

Introduction

Due to the implication of aryloxy radical intermediates [1] both in biological oxidations [2] and in the oxidation of phenolic stabilizers widely used in the polymer

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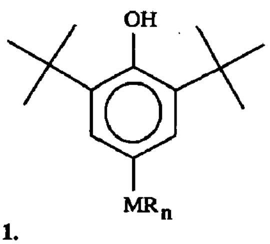
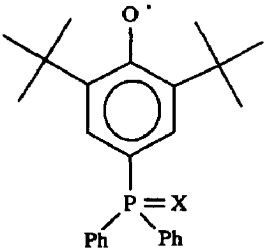


1.

a. M = S; R = Ph; n = 1
b. M = P; R = Ph; n = 2
c. M = Si; R = Me; n = 3
d. M = Se; R = Ph; n = 1
e. M = As; R = Ph; n = 2
f. M = N; R = H; n = 2
g. M = Sn; R = Ph; n = 3



2.

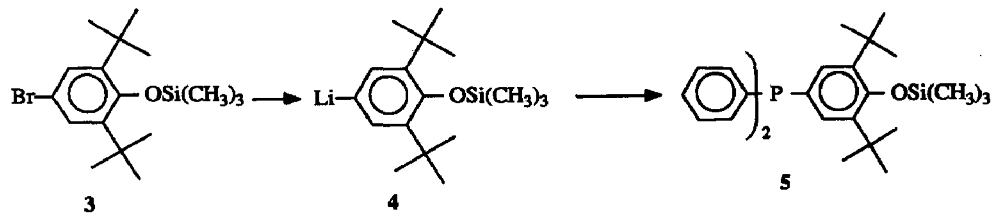
a. X = :
b. X = O
c. X = S

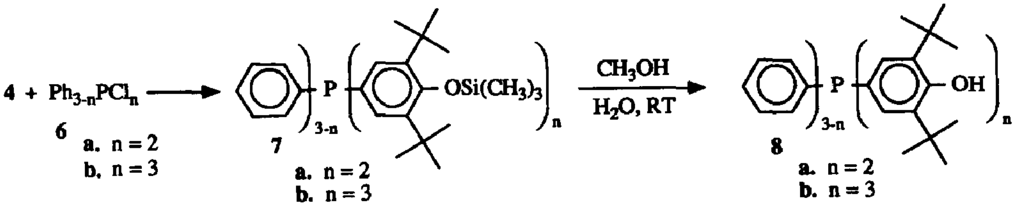
industry [3], the oxidation mechanism of hindered phenolics has received considerable attention in the literature. Particularly interesting have been studies directed towards ascertaining the degree of electron delocalization onto heteroatom substituents of aryloxy radicals [4]. Electron paramagnetic resonance studies have been reported in the aryloxy radicals of the sulfur [5], phosphorus [6], silicon [7], selenium [8], arsenic [9], nitrogen [10], and tin [11] derivatives **1a**–**1g**, respectively. The degree of unpaired-spin density on the phosphorus atom in **2a**–**2c** was found to be dependent both upon the oxidation state and the substituents on phosphorus [6].

The systematic study of electronic interactions of main-group elements substituted by more than one persistent aryloxy radical has been impeded by the lack of a general synthetic method for the preparation of the appropriate sterically hindered phenolic precursors. Previous methods including the substitution of 4-iodophenols by arsenides [9] or phosphides [6], reaction of either organomagnesium or organolithium reagents with phenolic disulfides [5] or diselenides, [8] and Wurtz-type coupling of 4-haloaryloxysilanes and halosilanes with metallic sodium [12] are not generally suitable for the preparation of derivatives containing more than one hydroxyaryl group. Our continued interest in the study of sterically hindered molecules of phosphorus [13] and silicon [14] led us to develop a general methodology for the preparation of 4-substituted derivatives of both phosphorus and silicon, which is reported herein.

Results and discussion

Unsubstituted tris(4-hydroxyphenyl)phosphines have been prepared by the reaction of the Grignard reagent derived from 4-bromoanisole with phosphorus trichloride followed by cleavage of the methyl ether with hydrobromic or hydroiodic acid [15]. This methodology cannot be extended to the preparation of sterically hindered phenolic derivatives with *ortho* t-butyl substituents because the acidic conditions required to cleave the methyl ether will result in either the partial or complete removal of the t-butyl substituents [16]. Quite recently, van Zon et al. described the *ortho* metalation of anisole followed by the reaction with dichlorophenylphosphine, **6a**, to give the bisadduct [17]. We anticipated that the lithiation of a protected sterically hindered 4-bromophenol with a protecting group that could be easily





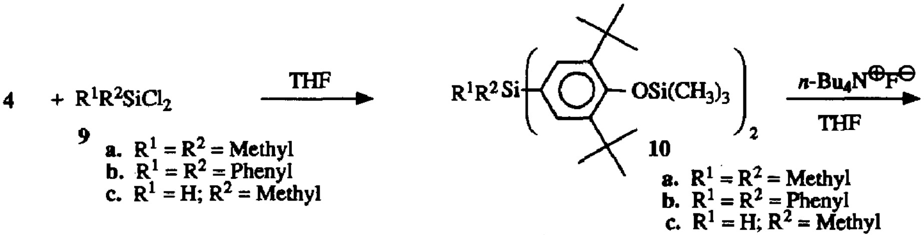
removed under mild conditions could be developed into a general method for the preparation of phenolic derivatives of the main-group elements.

Toward this end, the silyl-protected phenol **3** was prepared by the method of Moore [18]. The lithiated species **4** was prepared in situ by the transmetalation of a tetrahydrofuran (THF) solution of **3** with n-butyllithium at −78°C for 1 h. The addition of an equivalent of chlorodiphenylphosphine at −78°C followed by stirring at room temperature gave upon workup the trimethylsilyloxphenylphosphine **5** (41% HPLC). A significant quantity of the desired phenolic derivative **1b** was also obtained upon HPLC purification of the reaction product, which was no doubt due to the hydrolysis of **5** as the result of an aqueous extraction during workup. A corrected yield of 72% can be calculated for **5** based upon the quantity of **1b** obtained. The hydrolysis of the protected phenolic silanes could be easily avoided by employing a nonhydrolytic workup procedure.

In the $^{31}P\{^1H\}$ NMR spectra of **1b** and **5**, resonances were observed at −5.5 and −6.2, respectively, which are in the spectral region expected for a trivalent phosphine [19]. The spectral and elemental analyses were fully in accord with the structures illustrated.

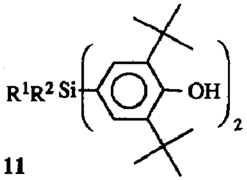
The protected 4-hydroxylarylphosphines **7a**, **7b** were obtained by the reaction of **4**, which was prepared in situ, with the corresponding chlorophosphines **6a**, **6b**. The bisadduct **8a** was easily obtained by deprotection of **7a**. The removal of the trimethylsilyl protecting group was accomplished by heating a solution of **7a** in a 12.5/1 mixture of methyl alcohol and water at reflux for 4 h. In the IR spectrum of **8a**, the expected absorption for the hindered phenolic OH group was observed at 3620 cm^{-1} and in the $^{31}P\{^1H\}$ NMR spectrum a resonance was observed at δ −5.4 that is in the region expected for a triarylphosphine. Surprisingly, the trisadduct **8b** could not be obtained in a pure state, although both the ^1H and ^{31}P NMR spectra had major resonances that could be assigned to **8b**. In the mass spectrum, a molecular ion was observed for **8b** at 646 mass units.

Extension of this methodology to prepare hindered bis(4-hydroxyaryl)silane derivatives proved to be straightforward. The reaction of **4** with dichlorodimethylsilane, **9a** gave the bisadduct **10a** as a white crystalline solid. The trimethylsilyl-pro-

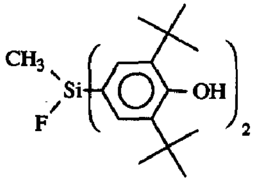


9
a. $R^1 = R^2 =$ Methyl
b. $R^1 = R^2 =$ Phenyl
c. $R^1 =$ H; $R^2 =$ Methyl

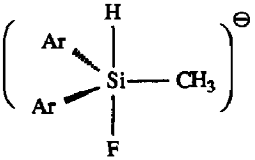
10
a. $R^1 = R^2 =$ Methyl
b. $R^1 = R^2 =$ Phenyl
c. $R^1 =$ H; $R^2 =$ Methyl



11
a. $R^1 = R^2 =$ Methyl
b. $R^1 = R^2 =$ Phenyl
c. $R^1 =$ H; $R^2 =$ Methyl



12



13

tecting group of **9a** was removed under aprotic conditions in THF (0–22° C) using *N,N,N,N*-tetra-n-butylammonium fluoride trihydrate (TBAF · trihydrate) [20] to give the bis(4-hydroxyphenyl)silane **11a**.

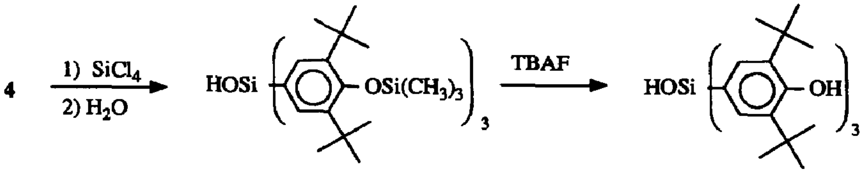
The structure of **11a** rests on the following observations. In the IR spectrum of **11**, a sharp absorption was observed at 3640 cm^{-1} which is characteristic of hindered phenolic hydroxyl groups, whereas the corresponding exchangeable singlet resonance was observed at δ 5.27 in the ^1H NMR spectrum. In the ^1H NMR spectrum, singlet resonances were observed at δ 0.52 and 1.46 that were assigned to the protons of the equivalent methyl groups attached to silicon and of the t-butyl groups, respectively. The spectral and elemental analysis were fully consistent with the structure illustrated.

In an analogous manner, the diphenyl derivative **11b** was prepared by the reaction of **4** with **9b** followed by deprotection of the trimethylsilyl ether **10b**. Although the Si–H bond is known to be reactive with both organomagnesium and organolithium reagents [21], the reaction of **4** with dichloromethylsilane, **9c**, gave **10c** in good yield (75% recrystallized). In the ^1H NMR spectrum of **10c**, a quartet resonance was observed at δ 4.90, which was assigned to the proton bonded to silicon.

The removal of the trimethyl protecting group of **10c** under the usual aprotic condition with TBAF · trihydrate, however, gave a low yield of the hindered phenolic derivative **11c**. During the addition of the TBAF · trihydrate to a solution of **10c** in THF, a vigorous evolution of gas was observed and the reaction mixture acquired a green coloration. Besides the desired **11c** that was obtained by preparative HPLC, the fluorosilane **12** was isolated. In the ^1H NMR spectrum of **12**, a doublet resonance was observed at 0.74 for the protons of the methyl group bonded to silicon coupled to fluorine (^3J(HCSiF) 7.0 Hz). The downfield shift of the protons of the methyl group bonded to silicon (δ 0.74) in **12** compared to the analogous protons in **11c** (δ 0.65) is consistent with the replacement of the hydrogen atom by a strongly electronegative fluorine atom. In the ^{19}F NMR spectrum, the expected quartet resonance was observed at δ −85.7.

A reasonable explanation for the formation of **12** involves the addition of fluoride anion to the silicon atom of **10c** (or the corresponding desilylated anion) to give a pentacoordinate trigonal bipyramidal intermediate (or transition state) **13** followed by loss of hydride [22*]. Substitution reactions at silicon are generally accepted to proceed through five-coordinate transitions states [23*,24*]. A similar mechanism has been suggested by Furin et al. for the fluoride promoted hydride transfer from silanes to carbonyl compounds [25*].

Eaborn has reported that the reaction of 2-propyl, cyclohexyl, and *o*-tolyl Grignard reagents with tetrafluorosilane gave the product of trisubstitution [26]. Not unexpectedly, the reaction of **4** with silicon tetrachloride gave upon aqueous workup the triarylsilanol **14**. Deprotection of **14** with TBFA gave the tris(4-hydroxyphenyl)silanol **15** as a white solid (46% recrystallyzed).



14 **15**

In summary, a general methodology has been developed for the synthesis of sterically hindered phenolic derivatives of both phosphorus and silicon. It is anticipated that this methodology can be readily extended to the preparation of other sterically hindered-phenolic metal and metaloid derivatives.

Experimental

All melting points were determined in open capillary tubes with a Thomas–Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer Model 1300 spectrophotometer, and reported peak absorptions are estimated to be accurate to ± 10 cm^{-1}. ^{1}H NMR spectra were taken on a JEOL FX-90Q, Varian Model CFT-20, or Varian Model XL-200 spectrometer. ^{19}F NMR and ^{31}P{^{1}H} NMR spectra were obtained on a Varian Model XL-200 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane where a positive sign is downfield from the standard. All ^{19}F chemical shifts are reported in ppm relative to trichlorofluoromethane. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. The abbreviations used for peak multiplicity are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, and dq = doublet of quartets. MS were obtained on a Finnigan Model 8200 mass spectrometer. Merck 9385 silica gel 60 (230–400 mesh) was used for flash chromatography [27]. Merck pre-coated (0.25 mm) silica gel 60 F-254 plates were used to TLC. Merck pre-coated (2.0 mm) silica gel 60 F-254 plates were used for preparative TLC. Preparative HPLC was carried out with a Waters PREP 500A HPLC on silica gel columns. Reagents were purchased from

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* Reference number with asterisk indicates a note in the list of references.

commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Tetrahydrofuran (THF) was distilled immediately prior to use from a deep-blue solution of sodium ketyl (sodium/benzophenone). Reactions were carried out in dried apparatus under a dry, inert atmosphere of either nitrogen or argon. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corp.

3,5-Di-t-butyl-4-trimethylsilyloxyphenyl(diphenyl)phosphine (5)

To a stirred suspension of 20.00 g (56 mmol) of **3** in 80 ml of THF at −78°C was added dropwise 38 ml (56 mmol) of a 1.55 *M* solution of n-butyllithium in hexane. The resulting homogeneous solution was stirred for 1 h at −78°C and then to the reaction mixture was added dropwise 12.36 g (56 mmol) of diphenylchlorophosphine. The reaction mixture was stirred for 24 h at room temperature and then the suspension of lithium chloride was removed by filtration. The solvent was removed in vacuo and the residue was dissolved in 250 ml of diethyl ether. The solution was extracted with water (3 × 250 ml) and the organic phase was dried over anhydrous sodium sulfate. The volatiles were removed in vacuo and the crude product was purified by preparative HPLC (99/1 heptane/ethyl acetate eluent) to give 10.70 grams (41%) of a white solid, m.p. 76–80°C; ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 9H), 1.46 (s, 18H), 7.08–7.61 (complex m, 12H); ^{31}P NMR (C_6D_6) δ −6.2. Anal. Found: C, 75.5; H, 8.6. $C_{29}H_{39}OPSi$ calcd.: C, 75.3; H, 8.5%.

Bis(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)phenylphosphine (7a)

Following the procedure used to prepare **5**, compound **7a** was prepared from 20.00 g (56 mmol) of **3**, 35 ml (56 mmol) of a 1.6 *M* solution of n-butyllithium in hexane, and 5.01 g (28 mmol) of **6a**. The residue was purified by preparative HPLC (silica gel, 99/1 heptane/ethyl acetate eluent) followed by recrystallization from methyl alcohol to give 7.20 g (29%) of a white solid, m.p. 129–131°C; ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 18H), 1.31 (s, 36H), 7.06 (s, 4H), 7.25 (complex m, 5H); ^{31}P NMR (C_6D_6) δ −7.0. Anal. Found: C, 72.4; H, 9.9. $C_{40}H_{63}O_2PSi_2$ calcd.: C, 72.5; H, 9.6%.

Tris(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)phosphine (7b)

Following the procedure used to prepare **5**, compound **7b** was prepared from 20.00 g (56 mmol) of **3**, 35 ml (56 mmol) of 1.6 *M* solution of n-butyllithium in hexane, and 2.56 g (18.7 mmol) of **6b**. The residue was triturated with acetonitrile to give 6.10 g (38%) of a white solid, m.p. 168–170°C; ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 27H), 1.33 (s, 54H), 7.08 (s, 6H); ^{31}P NMR (C_6D_6) δ −7.9. Anal. Found: C, 71.0; H, 10.6. $C_{51}H_{87}O_3PSi_3$ calcd.: C, 70.9; H, 10.2%.

3,5-Di-t-butyl-4-hydroxyphenyl(diphenyl)phosphine (1b)

During the purification of compound **5** by preparative HPLC (99/1 heptane/ethyl acetate eluent), 6.50 g of compound **1b** was isolated as a white solid, m.p. 92–93°C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 18H), 5.18 (exchangeable s, 1H), 7.11–7.55 (complex m, 12H); ^{31}P NMR (C_6D_6) δ −5.5. Anal. Found: C, 79.8; H, 8.1. $C_{26}H_{31}OP$ calcd.: C, 80.0; H, 8.0%.

*Bis(3,5-di-t-butyl-4-hydroxyphenyl)phenylphosphine (**8a**)*

A solution of 1.00 g (1.5 mmol) of **7a** and 2.0 g of water in 25 ml of methyl alcohol was heated at reflux temperature for 4 h. The solvent was removed in vacuo and the residue was purified by flash chromatography (9/1 heptane/ethyl acetate eluent) to give 0.30 g (35%) of a white solid, m.p. 138–140 °C; IR (CH_2Cl_2) ν 3620 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 36H), 5.21 (exchangeable s, 2H), 7.02–7.27 (complex m, 9H); ^{31}P NMR (C_6D_6) δ −5.4. Anal. Found: C, 78.3; H, 9.1. $C_{44}H_{47}O_2P$ calcd.: C, 78.7; H, 9.1%.

*Bis(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)dimethylsilane (**10a**)*

Following the procedure used to prepare **5**, compound **10a** was prepared from 5.00 g (14 mmol) of **3**, 8.75 ml (14 mmol) of 1.6 *M* solution of n-butyllithium in hexane, and 0.80 g (7 mmol) of **9a** in 20 ml of THF. The residue was recrystallized from heptane to give 1.50 g (33%) of a white solid, m.p. 173–174 °C; ^1H NMR ($CDCl_3$) δ 0.40 (s, 18H), 0.58 (s, $Si(CH_3)_2$, 6H), 1.38 (s, 36H), 7.38 (s, 4H). Anal. Found: C, 70.2; H, 1.08. $C_{36}H_{64}O_2Si_3$ calcd.: C, 70.5; H, 10.5%.

*Bis(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)diphenylsilane (**10b**)*

Following the procedure used to prepare **5**, compound **10b** was prepared from 20.00 g (56 mmol) of **3**, 35 ml (56 mmol) of 1.6 *M* solution of n-butyllithium in hexane, and 7.10 g (28 mmol) of **9b** in 100 ml of THF. The residue was purified by preparative HPLC (1/1 heptane/methylene chloride eluent) to give 5.00 g (24%) of a light yellow solid, m.p. 110–115 °C; ^1H NMR ($CDCl_3$) δ 0.40 (s, 18H), 1.40 (s, 36H), 7.40–7.80 (complex m, 14H). Anal. Found: C, 74.5; H, 9.5. $C_{46}H_{68}O_2Si_3$: C, 74.9; H, 9.3%.

*Bis(3,5-t-butyl-4-trimethylsilyloxyphenyl)methylsilane (**10c**)*

Following the procedure used to prepare **5**, compound **10a** was prepared from 20.00 g (56 mmol) of **3**, 35 ml (56 mmol) of 1.6 *M* solution of n-butyllithiun in hexane, and 3.20 g (28 mmol) of **9c** in 100 ml of THF. The residue was recrystallized from acetonitrile to give 12.50 g (75%) of a white solid, m.p. 119–121 °C; ^1H NMR ($CDCl_3$) δ 0.40 (s, 18H), 0.61 (s, $Si(CH_3)_2$, 6H), 1.40 (s, 36H), 4.90 (q, 1H), 7.40 (s, 4H); mass spectrum (direct probe) *m/z* 598 ($M^{+\cdot}$). Anal. Found: C, 69.8; H, 10.5. $C_{35}H_{62}O_2Si_3$ calcd.: C, 70.2; H, 10.4%.

*Bis(3,5-di-t-butyl-4-hydroxyphenyl)dimethylsilane (**11a**)*

To a solution of 9.80 g (16 mmol) of **10a** in 50 ml of THF was added slowly 10.60 g (32 mmol) of TBAF · trihydrate. The reaction mixture was stirred for 1 h at room temperature and then to it was added 0.80 g (14 mmol) of glacial acetic acid. The reaction mixture was poured into 250 ml of water and the resultant mixture was extracted with dichloromethane (2 × 125 ml). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed in vacuo. The residue was recrystallized from heptane to give 1.20 g (17%) of a white solid, m.p. 186–188 °C, IR (CH_2Cl_2) ν 3640 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.52 (s, $Si(CH_3)_2$, 6H), 1.46 (s, 36H), 5.27 (exchangeable s, OH, 2H), 7.40 (s, 4H). Anal. Found: C, 77.2; H, 10.7. $C_{33}H_{48}O_2Si$ calcd.: C, 76.9; H, 10.3%.

Bis(3,5-di-t-butyl-4-hydroxyphenyl)diphenylsilane (11b)

Following the procedure used to prepare **1a**, compound **11b** was prepared from 9.80 g (16 mmol) of **10b** and 10.60 g (32 mmol) of TBAF · trihydrate (added as a solution in 35 ml of THF) in 30 ml of THF (a solution of 2.20 g (62 mmol) of conc. hydrochloric acid in 10 ml of THF was used instead of glacial acetic acid). The residue was recrystallized from heptane to give 3.00 g (75%) of a white solid, m.p. 193–194.5 °C, ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 36H), 5.31 (exchangeable s, OH, 2H), 7.42–7.67 (complex m, 14H). Anal. Found: C, 81.1; H, 8.7. $C_{40}H_{52}O_2Si$ calcd.: C, 81.0; H, 8.3%.

Bis(3,5-di-t-butyl-4-hydroxyphenyl)methylsilane (11c)

Following the procedure used to prepare **11a**, compound **11c** was prepared from 6.00 g (10 mmol) of **10c** and 6.30 g (20 mmol) of TBAF · trihydrate (added as a solution in 35 ml of THF) in 30 ml of THF. The residue was purified by preparative HPLC 99/1 heptane/ethyl acetate eluent) to give 0.40 g (9%) of a white crystalline solid, m.p. 191–193.5 °C, ^{1}H NMR ($CDCl_3$) δ 0.65 (d, $SiCH_3$, 3H), 1.46 (s, 36H, 4.96 (q, SiH, 1H), 5.33 (exchangeable s, OH, 2H), 7.40 (s, 4H). Anal. Found: C, 76.7; H, 10.2. $C_{29}H_{46}O_2Si$ calcd.: C, 76.6; H, 10.2%.

Bis(3,5-di-t-butyl-4-hydroxyphenyl)methylfluorosilane (12)

During the isolation of compound **11c** by HPLC, 0.50 g of compound **12** was obtained as a white solid, m.p. 185–188 °C, ^{1}H NMR ($CDCl_3$) δ 0.74 (d, $SiCH_3$, ^3J(HCSiF) 7.0 Hz, 3H), 1.45 (s, 36H), 5.43 (exchangeable s, OH, 2H), 7.49 (s, 4H); ^{19}F NMR ($CDCl_3$) δ −85.7 (q, SiF, ^3J(FSiCH) 7.0 Hz). Anal. Found: C, 73.9; H, 9.8; F, 3.6. $C_{29}H_{45}FO_2Si$ calcd.: C, 73.7; H, 9.6; F. 4.0%.

Tris(3,5-di-t-butyl-4-trimethylsilyloxyphenyl)silanol (14)

Following the procedure used to prepare **5**, compound **14** was prepared from 20.00 g (56 mmol) of **3**, 35 ml (56 mmol) of 1.6 *M* solution of n-butyllithium in hexane, and 2.40 g (14 mmol) of silicon(IV) tetrachloride in 100 ml of THF. The residue was purified by preparative HPLC (96/4 heptane/ethyl acetate eluent) to give 2.80 g (22%) of a white solid, m.p. 192–196 °C; ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 27H), 1.39 (s, 54H), 7.57 (s, 6H); mass spectrum (direct probe) *m/z* 876 ($M^{+\cdot}$). Anal. Found: C, 70.3; H, 10.0. $C_{51}H_{88}O_4Si_4$ calcd.: C, 69.8; H, 10.1%.

Tris(3,5-di-t-butyl-4-hydroxyphenyl)silanol (15)

Following the procedure used to prepare **11a**, compound **15** was prepared from 0.40 g (0.45 mmol) of **14** and 0.43 g (1.37 mmol) of TBAF · trihydrate (added as a solution in 3 ml of THF) in 3 ml of THF. The residue was purified by preparative TLC followed by recrystallization from a mixture of heptane and toluene to give 0.14 g (46%) of a white solid, m.p. 257–258 °C; ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 54H), 2.26 (s, SiOH, 1H), 5.33 (s, OH, 3H), 7.55 (s, 6H); mass spectrum (direct probe) *m/z* 660 ($M^{+\cdot}$). Anal. Found: C, 75.9; H, 9.8. $C_{42}H_{64}O_4Si$ calcd.: C, 76.3; H, 9.8%.

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