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Novel One-Pot Synthesis of Aryltris(trimethylsilyl)silanes

Mahesh J. Sanganee,[†] Patrick G. Steel,*[,‡] and
Daniel K. Whelligan[‡]

*Department of Chemistry, University of Durham,
Science Laboratories, South Road Durham DH1 3LE, U.K.,
and Synthetic Chemistry, GlaxoSmithKline,
Gunnels Wood Road, Stevenage, Herts SG1 2NY, U.K.*

p.g.steel@durham.ac.uk

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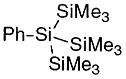
Abstract: The simple combination of tris(trimethylsilyl)-potassium, ArMgBr, and ArBr provides a novel "one-pot" synthesis of aryl(tristrimethylsilyl)silanes. A mechanistic rationale for this conversion is proposed.

In connection with a project investigating the use of silenes as reagents for organic synthesis,[1] we required multigram quantities of organotris(trimethylsilyl)silanes. Furthermore, to facilitate subsequent "Fleming−Tamao"-type oxidations, aryl derivatives were of particular interest. In addition to functioning as a bulky steric ("hypersilyl") substituent in synthetic applications,[2,3] aryl(tristrimethylsilyl)silanes have found widespread use in assorted structural, spectroscopic,[4−7] and photochemical studies.[8−12] Reflecting these applications, a number of preparative methods have been reported.[8,10,13−16] However, although **1** can be obtained, these involve either multiple steps, the use of hazardous reagents or intermediates or require extensive and difficult purification giving only modest overall yields. Consequently, we have sought an alternative synthesis of phenyltris(trimethylsilyl)silane **1** and, in this paper, report a simple one-pot procedure for the preparation of this and related aryltris(trimethylsilyl)silanes from readily available tetrakis(trimethylsilyl)silane.



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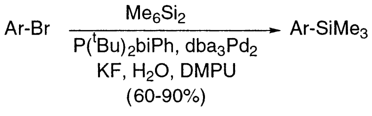
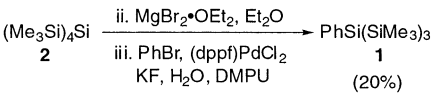
Recent reports by Goossen and Ferwanah have shown that trimethylsilylarenes can be conveniently prepared by a palladium-catalyzed silylation of aryl bromides using hexamethyldisilane, eq 1.[17]



$$\text{Ar-Br} \xrightarrow[\substack{\text{P(}^t\text{Bu)}_2\text{biPh, dba}_3\text{Pd}_2 \\ \text{KF, H}_2\text{O, DMPU} \\ (60\text{-}90\%)}]{\text{Me}_6\text{Si}_2} \text{Ar-SiMe}_3$$

[Eqn 1]

Our initial approach was to attempt this procedure replacing the disilane with commercially available tetrakis(trimethylsilyl)silane **2**.[18] However, all attempts to achieve this conversion, employing a variety of catalysts and conditions, afforded an intractable mixture of silylated aromatics. We speculate that the product is equally vulnerable to Si−Si bond activation by the palladium catalysts producing the observed product mixtures. This result suggested that if the reactivity of the original tris(trimethylsilyl)silane unit could be enhanced it would be possible to find conditions that allowed the efficient isolation of the desired silane **1**. Consequently, we explored the development of a silicon modification of the Hayashi procedure for the cross-coupling of Grignard reagents with aryl bromides.[19,20] Treatment of tetrakis(trimethylsilyl)silane with MeLi, according to the procedure of Gilman,[21] generated tris(trimethylsilyl)silyllithium which could be transmetalated with anhydrous $MgBr_2$ to produce the corresponding silyl-Grignard reagent, [$(Me_3Si)_3SiMgBr$]. Subsequently, we found that this procedure could be substantially accelerated and simplified by replacing MeLi with KO^tBu.[2] Following the Hayashi protocol, treatment of this Grignard reagent with bromobenzene in the presence of (dppf)$PdCl_2$ afforded the desired phenyltris(trimethylsilyl)silane **1** in 20% yield, eq 2.



$$\underset{\mathbf{2}}{(\text{Me}_3\text{Si})_4\text{Si}} \xrightarrow[\substack{\text{iii. PhBr, (dppf)PdCl}_2 \\ \text{KF, H}_2\text{O, DMPU}}]{\substack{\text{i. KO}^t\text{Bu, THF} \\ \text{ii. MgBr}_2\bullet\text{OEt}_2\text{, Et}_2\text{O}}} \underset{\substack{\mathbf{1} \\ (20\%)}}{\text{PhSi(SiMe}_3)_3}$$

[†] GlaxoSmithKline.

[‡] Durham University.

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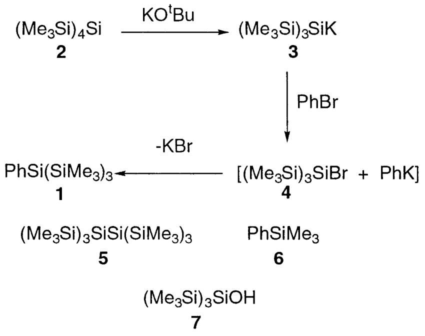
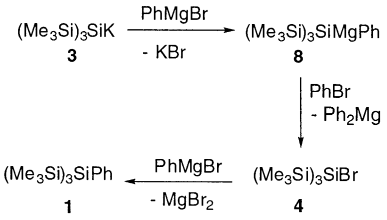
SCHEME 1



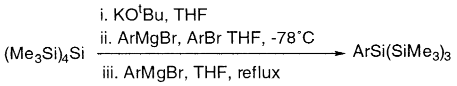
SCHEME 2



In attempts to optimize this process, a range of conditions, including alternative silylmetallics (organolithium, potassium, or magnesium reagent), catalysts, modes of addition, and temperatures were investigated. However, little benefit accrued. During these studies, it was observed that an initial reaction occurred on mixing the silyl organometallic and aryl bromide even in the absence of the catalyst. This suggested that **1** could be formed via a metal−halogen exchange between the initially formed silyl potassium **3** and bromobenzene to form silyl bromide **4** and phenylpotassium which then combine with elimination of KBr, Scheme 1. From GCMS analysis of the crude reaction mixture the alternative silanes **5**[22] and **6** were identified as the major side products in this process. These could arise from reaction of silylpotassium **3** with the bromide **4** and trimethylsilane abstraction by phenylpotassium, respectively. While use of the corresponding magnesium reagents minimized the latter problem, conversion of the silyl bromide was poor as ascertained by isolation of the corresponding silanol **7**.

Speculating that an additional aliquot of the aryl Grignard reagent would accelerate trapping of the intermediate bromide and thus reduce the amount of octasilane **5** formed, a mixture of silylpotassium **3** and 2 equiv of PhMgBr were combined to produce PhMgSi$(SiMe_3)_3$ and PhMgBr. Addition of aryl bromide then afforded the desired phenyltris(trimethylsilyl)silane **1** in 65% yield (GC) with minimal byproducts. Further refinements to this process involved portionwise addition of the aryl Grignard reagent and a final reflux to ensure complete displacement of the bromide. With these conditions a reproducible yield of 60−69% of the desired silane could be obtained on scales up to 20 g.

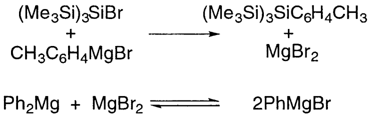
TABLE 1. Yields of Aryltris(trimethylsilyl)silane, $ArSi(SiMe_3)_3$



Ar	yield (%)
Ph (**1**)	70
Tol (**9**)	48
4-(MeO)C_6H_4 (**10**)	55
4-FC_6H_4 (**11**)	64
4-(F_3C)C_6H_4 (**12**)	31

We hypothesise that the reaction proceeds via initial reaction of the silyl potassium **3** with PhMgBr to precipitate KBr and generate tristrimethylsilyl(phenyl)magnesium **8**, Scheme 2.[23] This reacts rapidly, at low temperatures, with the aryl bromide to produce the silyl bromide **4**, as detected by GCMS, and relatively unreactive diarylmagnesium. Final substitution occurs on addition of the second equivalent of the Grignard reagent.

Attempts to intercept the intermediate silyl bromide using a different Grignard reagent, tolylmagnesium bromide, afforded a 3:7 mixture of phenyl- and tolyl-substituted products, respectively. This can be attributed to the Schlenk equilibria between Ph_2Mg and PhMgBr being accelerated by the magnesium bromide liberated in the final substitution step, eqs 3 and 4.[24,25]



$$\begin{matrix}(Me_3Si)_3SiBr\\+\\CH_3C_6H_4MgBr\end{matrix}\longrightarrow\begin{matrix}(Me_3Si)_3SiC_6H_4CH_3\\+\\MgBr_2\end{matrix}$$

$$Ph_2Mg + MgBr_2 \rightleftharpoons 2PhMgBr$$

Having established an optimal procedure for the preparation of **1**, we then explored its application to other substrates. Both electron-rich (4-MeO) and electron-poor (4-CF_3) aryl bromides prove to be viable substrates for this conversion, Table 1.

In conclusion, this process provides a convenient one-pot access to aryl(tristrimethylsilyl)silanes via a novel sequence of reactions. Efforts to further enhance this preparation and fully elucidate the mechanism of this process are in progress. Results of this and the studies of these reagents as silene precursors will be reported in due course.

Experimental Section

All reactions were carried out under an argon atmosphere in glassware dried under high vacuum by a heat-gun. THF was distilled from sodium benzophenone ketyl under nitrogen. All other reagents were used directly as supplied. Flash column chromatography was carried out using silica gel 40−60 mesh. High-resolution mass spectra were performed at the EPSRC service at the University of Swansea.

General Procedure As Applied to Phenyltris(trimethylsilyl)silane 1. Dry tetrakis(trimethylsilyl)silane[26] **2** (18.66 g, 58.31 mmol) and potassium *tert*-butoxide (6.87 g, 61.23 mmol) were combined under argon. Dry THF (280 mL) was added and

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(26) This reagent is widely used as an NMR standard and is commercially available but can be readily prepared on a multigram scale. See reference 18.

the solution stirred for 2 h after which time it was dark red. Phenylmagnesium bromide (1.0 M, 64.1 mL, 64.1 mmol) was added upon which a white precipitate formed. The mixture was stirred for 1 h and then cooled to −78 °C. Bromobenzene (9.2 mL, 87.5 mmol) was added quickly with rapid stirring causing a significant exotherm. After being stirred for a further 1 h at −78 °C, the mixture was warmed to rt for 30 min, and more phenylmagnesium bromide (1.0 M, 93.3 mL, 93.3 mmol) was added. The mixture was refluxed until GC showed the reaction complete. Saturated ammonium chloride solution (280 mL) was then added. The aqueous layer was separated and extracted with ether (3 × 280 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated, and dried in vacuo. Flash column chromatography on silica gel (petroleum ether) followed by Kugelrohr distillation afforded the title compound **1** as an amorphous semiclear solid (13.03 g, 69%): R_f (*n*-hexane) 0.74; bp 95 °C/0.1 mmHg (lit.[10] bp 132 °C/1.5 mmHg); mp 82.0−83.0 °C (lit.[8] mp 84−85 °C); ν_{max} (thin film) 3066 (CH, aromatic), 2954, 2896, 1430, 1250 (SiC) cm^{-1}; δ_H (300 MHz; $CDCl_3$) 7.46−7.42 (2 H, m), 7.26−7.23 (3 H, m), 0.22 (27 H, s); δ_C (63 MHz; $CDCl_3$) 136.56, 135.53, 127.68, 127.31, 1.17; δ_{Si} (99 MHz; $CDCl_3$) −12.79, −76.82; *m/z* (EI) 324 (M^+, 30), 309 ($M^+ - Me$, 12), 251 ($M^+ - SiMe_3$, 17), 236 ($M^+ - Me - SiMe_3$, 22), 191 (25), 174 ($M^+ - Ph - SiMe_3$, 70), 159 ($M^+ - Ph - SiMe_3 - Me$, 26), 135 (24), 73 (Me_3Si^+, 100); all data agree with the literature values.[13]

***p*-Tolyltris(trimethylsilyl)silane 9** (1.03 g, 48%): R_f (*n*-hexane) 0.79; bp 65−70 °C/0.04 mmHg; ν_{max} (thin film) 3064, 3029, 3013, 2949, 2893, 1495, 1440, 1394, 1245, 1085, 866, 834, 796, 746, 687 cm^{-1}; δ_H (500 MHz; $CDCl_3$) 7.35 (2 H, d, *J* = 8.0 Hz), 7.09 (2 H, d, *J* = 8.0 Hz), 2.32 (3 H, s), 0.22 (27 H, s); δ_C (126 MHz; $CDCl_3$) 136.99, 136.54, 131.22, 128.63, 21.33, 1.16; δ_{Si} (99 MHz; $CDCl_3$) −12.89, −77.46; *m/z* (GCEI) 338 (MH^+, 31), 323 ($M^+ - Me$, 12), 265 ($M^+ - SiMe_3$, 27), 250 (12), 249 (12), 234 (9), 205 (26), 191 (51), 174 (100), 159 (38), 149 (72); HRMS (EI) found M^+, 338.1738, $C_{16}H_{34}Si_4$ requires *M* 338.1738.

***p*-Methoxyphenyltris(trimethylsilyl)silane 10** (1.50 g, 55%): R_f (petroleum ether) 0.29 ν_{max} (thin film) 2949, 2894, 2834, 1592, 1562, 1496, 1461, 1441, 1395, 1273, 1244, 1180, 1089, 1034, 866, 833, 687 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.36 (2 H, d, *J* = 8.5 Hz), 6.84 (2 H, d, *J* = 8.5 Hz), 3.79 (3 H, s), 0.22 (27 H, s); δ_C (63 MHz; $CDCl_3$) 159.31, 137.70, 125.23, 113.68, 54.88, 1.15; δ_{Si} (99 MHz; $CDCl_3$) −12.94, −77.76; *m/z* (CI, NH_4^+) 355 (MH^+, 100), 339 ($M^+ - Me$, 2), 297 (3), 281 ($M^+ - SiMe_3$, 2), 264 (13); HRMS (EI) found M^+, 354.1684, $C_{16}H_{34}OSi_4$ requires *M* 354.1687.

***p*-Fluorophenyltris(trimethylsilyl)silane 11** (1.23 g, 64%): R_f (petroleum ether) 0.85; bp 72−75 °C/0.07 mmHg; ν_{max} (thin film) 2949, 2893, 1586, 1493, 1397, 1245, 1231, 1161, 1083, 865, 834, 746, 687, 624, 513 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 7.43−7.36 (2 H, m), 7.01−6.92 (2 H, m), 0.21 (27 H, s); δ_C (126 MHz; $CDCl_3$) 162.87 (d, *J* = 247.5 Hz), 137.95 (d, *J* = 7.3 Hz), 130.52 (d, *J* = 3.8 Hz), 114.95 (d, *J* = 19.7 Hz), 1.08; δ_F (376 MHz; $CDCl_3$) −114.98 (m); δ_{Si} (99 MHz; $CDCl_3$) −12.85, −76.84; *m/z* (GCEI) 342 (M^+, 76), 327 ($M^+ - Me$, 36), 269 ($M^+ - SiMe_3$, 8), 254 (32), 253 (30), 250 ($M^+ - SiMe_3 - F$, 48), 239 (45), 235 (48), 211 (33), 209 (42), 208 (39), 195 (61), 192 (100), 174 (100), 159 (79), 153 (79); HRMS (EI) found M^+, 342.1490, $C_{15}H_{31}FSi_4$ requires *M* 342.1487.

***p*-Trifluoromethylphenyltris(trimethylsilyl)silane 12** (0.68 g, 31%): ν_{max} (thin film) 2951, 2894, 1604, 1389, 1325, 1260, 1247, 1165, 1127, 1101, 1057, 1017, 835, 694 cm^{-1}; δ_H (500 MHz; $CDCl_3$) 7.57 (2 H, d, *J* = 8.0 Hz), 7.50 (2 H, d, *J* = 8.0 Hz), 0.24 (27 H, s); δ_C (126 MHz; $CDCl_3$) 141.90, 136.52, 129.36 (q, *J* = 32.3 Hz), 124.42 (q, *J* = 272.5 Hz), 124.08 (q, *J* = 3.3 Hz), 1.10; δ_F (282 MHz; $CDCl_3$) −63.20 (s); δ_{Si} (99 MHz; $CDCl_3$) −12.60, −75.79; *m/z* (GCEI) 392 ($M^+ + H$, 5), 304 (5), 300 (5), 259 (4), 245 (17), 230 (17), 203 (25), 193 (64), 174 (46), 159 (26), 145 (40), 131 (40); HRMS (EI) found M^+, 392.1456, $C_{16}H_{31}F_3Si_4$ requires *M* 392.1455).

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