

# Reactions of dilithiobutadienes with monochlorosilanes: Observation of facile loss of organic groups from silicon

Paul F. Hudrlik \*, Donghua Dai, Anne M. Hudrlik

Department of Chemistry, Howard University, 525 College Street, N.W., Washington, DC 20059, United States

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## Abstract

Reactions of 1,4-dilithiobutadienes (from 1,4-diiodo-1,2,3,4-tetraethylbutadiene (**1**) and 2,2'-dibromobiphenyl (**7**) with *t*-BuLi) with Me<sub>3</sub>SiCl gave siloles (**3** and **9a**) as the major products. No evidence for a disilylated butadiene was obtained. Use of higher molecular weight chlorosilanes ((allyl)Me<sub>2</sub>SiCl, BnMe<sub>2</sub>SiCl, and PhMe<sub>2</sub>SiCl) with dibromide **7** gave dimethylsilole **9a** and a silane (**10a**, **10b**, or **10c**) resulting from trapping of the organic group by the chlorosilane.

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**Keywords:** Silole; Chlorosilane; Dilithiobutadiene; Organosilicon; Pentacoordinate silicon

## 1. Introduction

Siloles [1–4] (silacyclopentadienes) are of interest because of the aromaticity of some of their anions [2b,2c,2d,2e,2f,2g,2h,2i,2j,2k], as ligands in transition metal chemistry [3], and because their electronic properties suggest that silole-containing polymers (especially polysiloles) could be useful in materials chemistry [4]. One of the common ways of preparing siloles (and other metalloles) is by reaction of a 1,4-dimetallobutadiene [5] with a dihalo- (or tetrahalo-) silane. 1,4-Dilithiobutadienes are often generated from 1,4-di-iodobutadienes, easily prepared from zirconacyclopentadienes [6–8]. In the course of preparing some siloles to explore their potential use in organic synthesis, we used the reactions of 1,4-diiodotetraethylbutadiene (**1**) with alkylolithium reagents followed by chlorosilanes. In order to characterize the presumed 1,4-dilithiobutadiene intermediate (**5**), we attempted to trap it with Me<sub>3</sub>SiCl, expecting to obtain the 1,4-bis(trimethylsilyl) derivative **6**. We saw no evidence for the formation of **6**; instead, the major product was silole **3**. We therefore decided to also explore the cor-

responding reactions of 2,2'-dibromobiphenyl (**7**), which led to the dibenzosilole **9a**.

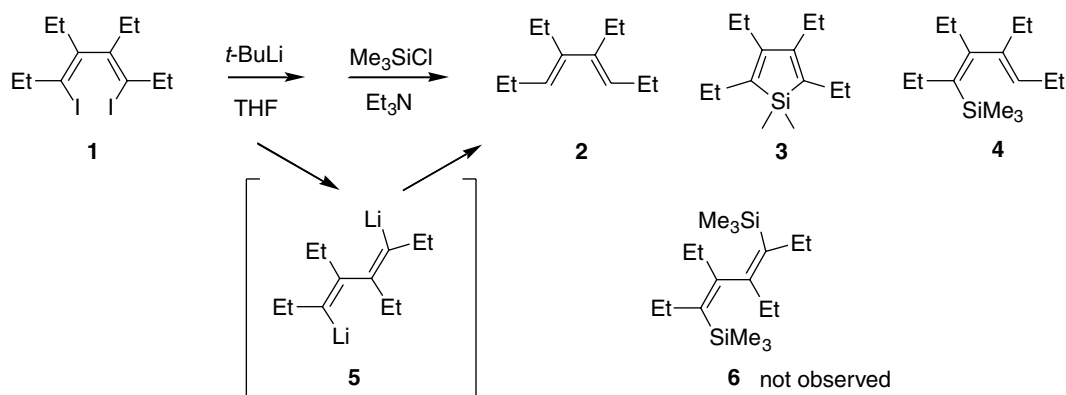
## 2. Results

### 2.1. 2,3,4,5-Tetraethylsilole series

The starting diiodo compound **1** was prepared by iodination of a zirconacyclopentadiene intermediate [2f,6,7] generated from 3-hexyne. Treatment of **1** with *t*-BuLi in THF generated the dilithio intermediate **5**, as shown by reaction with water or MeOH to give tetraethylbutadiene **2** [7]. However, when **5** was treated with Me<sub>3</sub>SiCl/Et<sub>3</sub>N [9], silole **3** was the major product (Scheme 1). Diene **2** and trimethylsilyltetraethylbutadiene **4** were identified as the major byproducts by GC/MS. No significant amount of higher retention time material was observed.

Silole **3** was most likely formed in the Me<sub>3</sub>SiCl reaction by cyclization of a monolithio monotrimethylsilylbutadiene intermediate with loss of MeLi. The MeLi would be expected to react with the excess Me<sub>3</sub>SiCl to form Me<sub>4</sub>Si. Therefore, in one experiment the reaction mixture was warmed to 42 °C, and the volatiles were passed into a vial containing CDCl<sub>3</sub> at –15 °C. <sup>1</sup>H NMR analysis of the CDCl<sub>3</sub> showed a peak at δ –0.005 (in addition to peaks

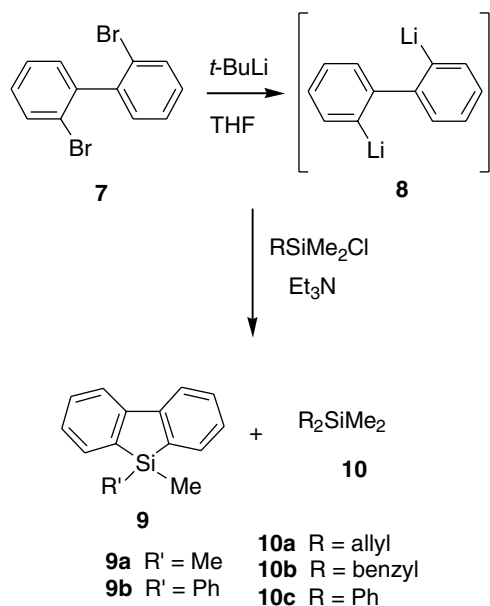
\* Corresponding author. Tel.: +1 202 806 4245; fax: +1 202 806 5442.  
E-mail address: phudrlik@howard.edu (P.F. Hudrlik).



from THF and pentanes), which disappeared when the solution was concentrated to half its volume, consistent with the formation of  $\text{Me}_4\text{Si}$ . Silole **3** did not appear to be very stable to aqueous workup, and in the presence of aqueous acid, it began to decompose, forming a compound having a somewhat higher retention time on GC, probably a ring-opened silanol.

## 2.2. Dibenzosilole series

These reactions were further studied using the dibenzosilole (silafluorene) system, since in our hands, these siloles were more robust than those from the tetraethyl system. Treatment of 2,2'-dibromobiphenyl (**7**) with *t*-BuLi in THF followed by excess  $\text{Me}_3\text{SiCl}$  in  $\text{Et}_3\text{N}$  gave silole **9a** as the major product, isolated by chromatography in 84% yield (Scheme 2). Again, there was no evidence for the formation of a bis(trimethylsilyl) compound. We did not attempt to trap the  $\text{Me}_4\text{Si}$  which must have been formed.



Similar reactions were carried out using several additional monochlorosilanes. In these reactions, the dibenzosilole (**9a**) was again formed as a major product, and the silanes (**10**) from cleavage-trapping were observed by NMR (and in some cases MS), and silanes **10b** and **10c** were isolated.

Thus, treatment of 2,2'-dibromobiphenyl (**7**) with *t*-BuLi in THF followed by excess allyldimethylchlorosilane in  $\text{Et}_3\text{N}$  gave a mixture of silole **9a** and diallyldimethylsilane (**10a**) by GC analysis and by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. In one experiment, the crude product was chromatographed, and silole **9a** was isolated in 68% yield. NMR yields were obtained (using nitromethane as a standard) of 95–103% for **9a** and 94–97% for **10a**.

Treatment of **7** with *t*-BuLi in THF followed by excess benzyldimethylchlorosilane in  $\text{Et}_3\text{N}$  gave a mixture of silole **9a** and dibenzyldimethylsilane (**10b**) by GC analysis, and by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. GC/MS analysis showed mass spectral evidence for silole **9a** and silane **10b** as well as a small amount of biphenyl (presumably from protonation of **8**). Pure samples of **9a** and **10b** were obtained by column chromatography. In some experiments, NMR yields were obtained (using nitromethane as a standard) of 81–100% for **9a** and 34–40% for **10b**.

Treatment of **7** with *t*-BuLi in THF followed by excess phenyldimethylchlorosilane in  $\text{Et}_3\text{N}$  gave a mixture of silole **9a** and diphenyldimethylsilane (**10c**), together with smaller amounts of 1-methyl-1-phenyldibenzosilole (**9b**), resulting from loss of methyl rather than phenyl. Compounds **9a**, **9b**, and **10c** were all observed in the crude product by GC, GC/MS and NMR. In addition, small amounts of  $\text{PhMe}_2\text{Si-}t\text{-Bu}$ , biphenyl, and bis(phenyldimethyl)disiloxane (**11c**) were identified by GC/MS. Pure samples of silole **9a** and silane **10c** were obtained by column chromatography followed by preparative GC, and a somewhat impure sample of silole **9b** was isolated by column chromatography. In some experiments, NMR yields were obtained (using nitromethane as a standard) of 66–72% for **9a**, 20–32% for **9b**, and 53–60% for **10c**.

Authentic samples of siloles **3** and **9a**, the silane cleavage-trapping products (**10a**, **b**, **c**), and the disiloxane hydrolysis products (**11a**, **b**, potential impurities) were

independently synthesized for GC and spectral comparisons, and a commercial sample of **11c** was available. The assignment of silole **9b** was based on the mass spectrum, and on the  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) which was comparable to that reported [10] (in  $\text{CCl}_4$ ); in particular the Si–Me of **9b** was found at  $\delta$  0.72 (this work) and  $\delta$  0.71 (reported).

### 3. Discussion

The formation of siloles **3** and **9a** from the presumed dilithio intermediates **5** and **8** and the monochlorosilanes most likely occurs via cyclization of a monolithio-monosilyl intermediate e.g., **12**, **14** to a pentacoordinated organosilicate such as **13** or **15** (Scheme 3). Pentacoordinated silicon compounds are well known, but most examples involve one or more electronegative groups attached to the silicon [11], and pentaorganosilicates are rare. Recently some have been observed by NMR [12,13], and a few have been isolated and characterized by X-ray crystallography [13]. Many of these are based on the silole nucleus.

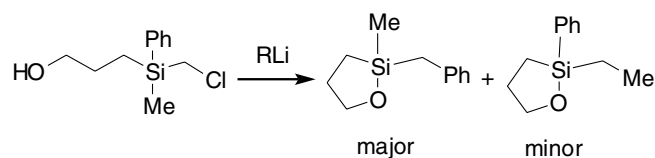
Gilman has reported some reactions of dibenzosiloles which probably involve pentaorganosilicon intermediates [14]. In 1953, Gilman and Gorsich reported the reaction of **8** with 1-chloro-1-methyldibenzosilole to give a mixture of silole **9a** (36%) and 1,1'-spirobi[dibenzosilole] (38%) [14b]. They proposed that this reaction involved the generation of methyllithium, which reacted with the starting chlorosilane. They also observed some reactions of **8** with  $\text{RSiCl}_3$  to give small amounts of the same spiro compound. However, the reactions of **8** with  $\text{Et}_3\text{SiCl}$  did not give the corresponding diethyldibenzosilole.

In 1983, Ishikawa and co-workers reported that several dibenzosiloles, including **9a**, react with organolithium

reagents to form products of exchange of alkyl groups on the silicon, and they proposed a pentacoordinate organosilicate intermediate [10,15]. Klumpp and co-workers were the first to observe an intermediate of this type by NMR [12a,12b]. They showed that **15** ( $\text{R} = \text{Me}$ ) could be generated from the organolithium derived from 2-bromo-2'-trimethylsilylbiphenyl and that it lost MeLi reversibly when warmed.

Recently Xi and co-workers reported the reactions of a number of 1-bromo-4-silyl butadienes with *t*-BuLi, which give siloles in good yields, accompanied by the cleavage of C–Si bonds [16]. The RLi which was generated was trapped by reaction with carbonyl compounds. The following selectivity for cleavage was demonstrated:  $\text{Me} \gg i\text{-Pr}$ ,  $\text{Ph} > \text{Me}$ , and  $\text{vinyl} > \text{Me}$ .

The reactions of **8** with  $\text{PhMe}_2\text{SiCl}$  gave a mixture of **9a** and **9b** (as well as **10c**), indicating formation of both PhLi (major) and MeLi (minor). This is in accord with the recent work of Xi and co-workers [16], and is also reminiscent of the alkoxide-induced rearrangements we studied some years ago, where the predominant phenyl migration was accompanied by a small amount of methyl migration [17].

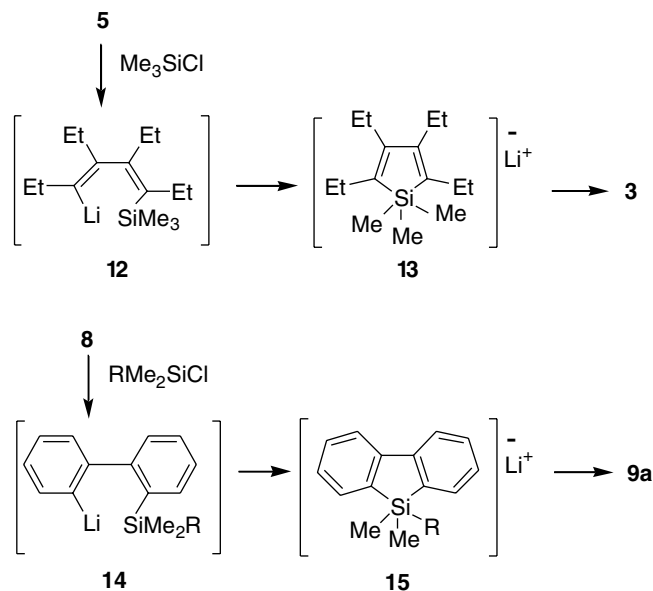


In the present work, the loss of the organic group (methyl, allyl, benzyl, or phenyl) from **13** or **15** most likely takes place by loss of RLi, but direct reaction of the chlorosilane with **13** or **15** is also a possibility. The novel aspect of the present work is that the uncyclized organolithium reagent (**12** or **14**) is not trapped by the excess chlorosilane. The fact that cyclization (to **13** or **15**) occurs instead of disilylation may be further evidence for the stability of pentaorganosilicate anions based on the silole nucleus [18].

### 4. Experimental

**General.** All reactions were run under argon, and transfers of liquids were carried out with argon-flushed syringes for all reactions except the preparation of siloxanes **11a** and **11b**. Low temperature reactions were cooled with either a petroleum ether or hexanes/liquid nitrogen slush bath, and the temperatures were measured using a thermometer placed beside the flask. Glassware was dried overnight in an oven at  $120^\circ\text{C}$ , and cooled in a desiccator. The verb “concentrated” refers to removal of solvent using a rotary evaporator. Column chromatography was done as flash chromatography [19] using 200–425 mesh silica gel.

NMR spectra were obtained in  $\text{CDCl}_3$  and are referenced to chloroform ( $\delta$  7.26,  $^1\text{H}$ ;  $\delta$  77.00,  $^{13}\text{C}$ ) unless otherwise indicated. Spectra recorded in benzene- $d_6$  were referenced to benzene ( $\delta$  7.15,  $^1\text{H}$ ;  $\delta$  128.00,  $^{13}\text{C}$ ). Analytical gas chromatography (GC) analyses were performed using a flame ionization detector with the following columns and



Scheme 3.

conditions: (A) 10% OV-101 silicone on 80/100 mesh Gas-Chrom Q; 2.6 m × 2.5 mm glass column: A1: 100 °C, 10 °C/min to 270 °C; A2: 100 °C, 10 °C/min to 250 °C; A4: 200 °C, 10 °C/min to 250 °C; and (B) Supelco SPB-1 (bonded polydimethylsiloxane), 30 m × 0.25 mm × 0.25 μm capillary column: B1: 200 °C, 10 °C/min to 270 °C; B2: 200 °C, 10 °C/min to 270 °C. Preparative GC was performed using a thermal conductivity detector.

**Materials.** Tetrahydrofuran (THF) and anhydrous ether were distilled from sodium/benzophenone under nitrogen. Et<sub>3</sub>N, Me<sub>3</sub>SiCl, and Me<sub>2</sub>SiCl<sub>2</sub> were distilled from calcium hydride. *n*-Butyllithium was obtained from Acros, and *tert*-butyllithium was obtained from Acros and from Alfa Aesar.

The chlorosilane/Et<sub>3</sub>N mixtures were prepared by centrifuging (3 min) a mixture of equal volumes of the chlorosilane and Et<sub>3</sub>N in an argon-flushed centrifuge tube (capped with a septum) and taking the supernatant solution by gas-tight syringe. The supernatant solutions were clear and almost colorless or light yellow. In two of the early experiments (isolation of silole **3** from both the Me<sub>2</sub>SiCl<sub>2</sub> and Me<sub>3</sub>SiCl procedures), the chlorosilane/Et<sub>3</sub>N mixture was not centrifuged, but was stored in the dark for several days to allow the precipitate to settle.

Diiodide **1** [2f,6] was prepared by iodine treatment [8a,8c] of the intermediate from Cp<sub>2</sub>ZrCl<sub>2</sub>, *n*-BuLi, 3-hexyne [6,7], and CuCl [6b]. Dibromide **7** was prepared from *o*-dibromobenzene by treatment with *n*-BuLi in THF [20].

#### 4.1. Authentic comparison samples

Silanes **10a** [22], **10b** [23], and **10c** [24], and siloxanes **11a** [25] and **11b** [26] were prepared as follows, and purified by Kugelrohr distillation: **10a** [(allyl)Me<sub>2</sub>SiCl (2.0 mmol), THF, (allyl)MgBr (2.1 mmol) in Et<sub>2</sub>O, r.t. 30 min, 70 °C 30 min]; **10b** [BnMe<sub>2</sub>SiCl (2.2 mmol), THF, BnMgCl (from 0.50 mL of BnCl and 0.262 g of Mg in ether), r.t. 30 min, 98% yield]; **10c** [PhMe<sub>2</sub>SiCl (2.3 mmol), THF, PhLi (2.3 mmol, 1.8 M in 70:30 cyclohexane:ether), r.t., 1.5 h, 93% yield]; **11a** [(allyl)Me<sub>2</sub>SiCl (2.7 mmol), excess aqueous NaHCO<sub>3</sub>, r.t. 10 min, 88% yield]; **11b** [BnMe<sub>2</sub>SiCl (2.2 mmol), excess aqueous NaHCO<sub>3</sub>, r.t. 10 min, 99% yield]. Compounds **10a**, **10c**, and **11a** were obtained as colorless oils having <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra consistent with those reported. Compound **10b** was obtained as a white solid: m.p. 52.0–54.3 °C (lit. [23b] m.p. 56–58 °C); <sup>1</sup>H NMR (400 MHz) δ 7.24 (crude t, 4H), 7.10 (crude t, 2H); 7.01 (crude d, 4H), 2.12 (s, 4H), –0.04 (s, 6H); <sup>13</sup>C NMR (100 MHz) δ 139.85, 128.19, 128.17, 124.03, 25.17, –3.88. The <sup>1</sup>H NMR spectrum is in line with those reported [23]. Compound **11b** was obtained as a colorless oil: <sup>1</sup>H NMR (400 MHz) δ 7.22 (crude t, 4H), 7.09 (crude t, 2H), 7.01 (crude d, 4H), 2.08 (s, 4H), 0.01 (s, 12H); <sup>13</sup>C NMR (100 MHz), 139.38, 128.31, 128.11, 124.02, 28.51, –0.10. The <sup>1</sup>H NMR spectrum was consistent with a reported spectrum of **11b** taken in CCl<sub>4</sub> [26].

1,1-Dimethyl-2,3,4,5-tetraethyl-1-silole (**3**) [16,27] was prepared from 0.3380 g (0.81 mmol) of diiodide **1** in 4 mL of anhydrous ether cooled to –64 °C, and 0.65 mL (1.63 mmol) of *n*-BuLi (2.5 M in hexanes) (then warmed to 10 °C over 45 min, and then cooled to –64 °C) followed by 0.20 mL (~0.82 mmol of chlorosilane) of a mixture of equal volumes of Me<sub>2</sub>SiCl<sub>2</sub> and Et<sub>3</sub>N in 4 mL of THF (dropwise). The mixture was warmed to r.t. over 45 min, stirred at r.t. for 1 h; then 12 mL of pentanes was added, and stirring was continued for 1 h. The liquid was cannulated into another flask through a sintered glass funnel, the filtrate was concentrated, pentanes was added, and the pentane soluble material was analyzed by GC (A1, C<sub>20</sub>H<sub>42</sub> at 19.2 min) showing the major peak at 9.7 min (75%, **3**) and two minor peaks at 6.4 min (5%, **2**) and 10.7 min (6%). The crude product (0.2300 g) was purified by preparative GC giving a sample of silole **3** as a light yellow oil. The <sup>1</sup>H and <sup>13</sup>C NMR spectra (300 MHz, benzene-*d*<sub>6</sub>) were equivalent to those reported below (400 MHz, benzene-*d*<sub>6</sub>), and the <sup>1</sup>H NMR spectrum was consistent with a reported spectrum of **3** taken in CCl<sub>4</sub> [27]. Silole **3** appeared to be unstable in CDCl<sub>3</sub>.

In a separate experiment, a <sup>1</sup>H NMR yield of 58% was calculated for **3** by adding a nitromethane standard, and integrating peaks for Si–CH<sub>3</sub> of **3** at δ 0.22 and for CH<sub>3</sub>NO<sub>2</sub> at δ 3.12 (chemical shifts relative to residual benzene at δ 7.15).

1,1-Dimethyldibenzosilole (**9a**) [2i,2j,14,21] was prepared from 0.2779 g (0.89 mmol) of dibromide **7** in 4 mL of anhydrous ether cooled to –66 °C, and 0.73 mL (1.8 mmol) of *n*-BuLi (2.5 M in hexanes) (dropwise; then warmed to r.t. over 30 min; then cooled to –67 °C) followed by 0.23 mL (~0.95 mmol of Me<sub>2</sub>SiCl<sub>2</sub>) of a mixture of equal volumes of Me<sub>2</sub>SiCl<sub>2</sub> and Et<sub>3</sub>N in 4 mL of THF (dropwise). The mixture was warmed to r.t. over 25 min, and stirred at r.t. for 2 h, the volatiles were removed by oil pump vacuum, and the residue was mixed with water and extracted with ether. The combined extracts were analyzed by GC (B2, C<sub>22</sub>H<sub>46</sub> at 7.5 min) and showed the major peak at 4.2 min (100%, **9a**). The product was concentrated, and placed under oil pump vacuum to give 0.1879 g (100% crude yield) of the dibenzosilole **9a** as a light yellow solid having <sup>1</sup>H and <sup>13</sup>C NMR spectra consistent with the reported spectra [2i,2j].

#### 4.2. NMR yields

NMR yields for silanes **10a**, **b**, and **c** and for silole **9a** were obtained as follows. The crude product was dissolved in CDCl<sub>3</sub>, and a measured amount (10–20 μL) of distilled nitromethane was added. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were taken to confirm the presence of the silane (**10a**, **b**, or **c**) and silole **9a**. The <sup>1</sup>H NMR (400 MHz) yields were calculated based on the integration of nitromethane (set at δ 4.24) relative to Si–CH<sub>3</sub> peaks at δ 0.40 (**9a**), 0.73 (**9b**), –0.015 (**10a**), and 0.55 (**10c**), and the CH<sub>2</sub> peak at 2.08 (**10b**). Other diagnostic peaks: **10b** (–0.12), **11a**, (0.054),

**11b** (−0.08, 2.04), **11c** (0.33). To confirm peak assignments, the NMR samples were then spiked with the authentic sample of silane (**10a**, **b**, or **c**) and then with that of the corresponding siloxane (**11a**, **b**, or **c**). For silole **9b**, the NMR sample was spiked with the purified sample of **9b** (see below).

#### 4.3. Treatment of 1,4-diiodo-1,2,3,4-tetraethylbutadiene (**1**) with *t*-BuLi followed by $\text{Me}_3\text{SiCl}$ : methyl as a leaving group

A solution of 0.2773 g (0.66 mmol) of diiodide **1** in 5 mL of THF was cooled to  $-56^\circ\text{C}$ , and 1.80 mL (2.9 mmol) of *t*-BuLi (1.6 M in pentane) was added. The solution was stirred at about  $-60^\circ\text{C}$  for 1 h. Then 0.50 mL of a mixture of equal volumes of  $\text{Me}_3\text{SiCl}$  and  $\text{Et}_3\text{N}$  ( $\sim 2.0$  mmol of chlorosilane) was added dropwise. The resulting mixture was warmed to r.t. over 40 min, and stirred at r.t. for 1.5 h. Then 5 mL of  $\text{CCl}_4$  (distilled from  $\text{P}_2\text{O}_5$ ) was added to the reaction mixture to give a yellow solution with a white precipitate, and stirring was continued for 15 min. Stirring was stopped, and after the solid settled down, the supernatant was cannulated to another flask. The volatile material was removed by oil pump vacuum, and pentanes was added to the flask. The pentane-soluble material was transferred to another flask via a cannula. GC analysis (A1) showed the major peak at 9.7 min (66%, **3**), and minor peaks at 6.4 min (7%, **2**) and 10.4 min (16%, **4**).

The major component was purified by preparative GC to give silole **3** as a colorless liquid. (GC analysis (A1) showed a major peak at 9.9 min (99%):  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ):  $\delta$  2.32 (q,  $J = 7.6$  Hz, 4H), 2.23 (q,  $J = 7.6$  Hz, 4H), 1.08 (t,  $J = 7.6$  Hz, 6H), 0.98 (t,  $J = 7.5$  Hz, 6H); 0.23 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz, benzene- $d_6$ ):  $\delta$  153.65, 138.27, 22.48, 21.04, 15.65, 15.00,  $-3.26$ . The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are equivalent to those of the sample prepared from **1** and  $\text{Me}_2\text{SiCl}_2$  (which were recorded at 300 MHz), and the GC retention times of the two samples were identical.

A GC/MS was obtained on the product from a separate experiment run using a larger excess of  $\text{Me}_3\text{SiCl}/\text{Et}_3\text{N}$ , and with a slightly different workup. GC analysis (A2) showed major peaks at 6.4 min (54%, **2**), 9.6 min (22%, **3**), and 10.4 min (17%, **4**). No other significant peaks were seen up to 25 min; under these conditions,  $\text{C}_{20}\text{H}_{42}$  came at 20.9 min. GC/MS showed major peaks at 6.5 min (MS corresponded to tetraethylbutadiene **2** [7a]), 8.2, and 8.5 min. The peak at 8.2 min showed  $m/z$  222 (100,  $\text{M}^+$ ), 207 (24,  $\text{M}^+ - \text{Me}$ ), 193 (44,  $\text{M}^+ - \text{Et}$ ), 163 (64), and was assigned as silole **3**. The peak at 8.5 min showed  $m/z$  238 (18,  $\text{M}^+$ ), 223 (6,  $\text{M}^+ - \text{Me}$ ), 209 (2,  $\text{M}^+ - \text{Et}$ ), 135 (53), 73 (100,  $\text{Me}_3\text{Si}^+$ ), and was assigned as 1-trimethylsilyltetraethylbutadiene **4**.

In a separate experiment (0.2081 g (0.50 mmol) of **1**, 2.25 mmol of *t*-BuLi, 0.50 mL of  $\text{Me}_3\text{SiCl}/\text{Et}_3\text{N}$ , GC analysis (A2) of the crude product before concentration showed the major peak at 9.7 min (72%, **3**) and a minor peak at 10.4 min (10%, **4**). The solution was concentrated, and then

placed under oil pump vacuum to give 0.1107 g of a yellow oil. Then 10.0  $\mu\text{L}$  (0.183 mmol) of nitromethane and 10.0  $\mu\text{L}$  (0.102 mmol) of ethyl acetate, together with 0.75 mL of benzene- $d_6$  were added.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR showed peaks corresponding to silole **3**. From the  $^1\text{H}$  NMR, an NMR yield based on integration with nitromethane was calculated for **3** to be 54%. The NMR yield was based on the Si- $\text{CH}_3$  peak of **3** at  $\delta$  0.21 and  $\text{CH}_3\text{NO}_2$  at  $\delta$  3.05 relative to residual benzene at  $\delta$  7.15.

#### 4.4. Treatment of 2,2'-dibromobiphenyl (**7**) with *t*-BuLi followed by $\text{Me}_3\text{SiCl}$ : methyl as a leaving group

A solution of 0.2719 g (0.87 mmol) of 2,2'-dibromobiphenyl (**7**) in 6 mL of THF was cooled to  $-70^\circ\text{C}$ , and 2.5 mL (3.8 mmol) of *t*-BuLi (1.5 M in pentane) was added. The resulting mixture was stirred between  $-69$  and  $-56^\circ\text{C}$  for 1 h and 20 min. Then 1.0 mL of a mixture of equal volumes of  $\text{Me}_3\text{SiCl}$  and  $\text{Et}_3\text{N}$  ( $\sim 4.0$  mmol of chlorosilane) was added. The mixture was warmed to r.t. over 40 min, and stirred at r.t. for 1 h 15 min.

Methanol ( $\sim 2$  mL) was added, and the mixture was stirred for 15 min. Then 2 mL of saturated  $\text{NaHCO}_3$  was added, and the resulting mixture was added to additional saturated  $\text{NaHCO}_3$ , and extracted with ether ( $2 \times 20$  mL, 10 mL). GC analysis (B1) of the combined extracts showed peaks at 4.1 min (6%) and 4.2 min (92%). The solution was dried ( $\text{Na}_2\text{SO}_4$ ), concentrated, and chromatographed (hexanes) to give 0.1544 g (84% yield) of silole **9a** as a white solid: m.p.  $55.5$ – $58.1^\circ\text{C}$  (lit. [14a] m.p.  $60$ – $61^\circ\text{C}$ ); GC analysis (B1) 4.2 min (99.8%). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and GC retention time were identical with those of **9a** obtained from  $\text{Me}_2\text{SiCl}_2$  (above).

#### 4.5. Treatment of 2,2'-dibromobiphenyl (**7**) with *t*-BuLi followed by allyldimethylchlorosilane: allyl as a leaving group

A solution of 0.2866 g (0.92 mmol) of 2,2'-dibromobiphenyl (**7**) in 6 mL of THF was cooled to  $-70^\circ\text{C}$ , and 2.7 mL (4.1 mmol) of *t*-BuLi (1.5 M in pentane) was added. The resulting mixture was stirred at  $-75$  to  $-60^\circ\text{C}$  for 1 h. Then 0.85 mL of a mixture of equal volumes of allyldimethylchlorosilane and  $\text{Et}_3\text{N}$  ( $\sim 2.8$  mmol of chlorosilane) was added. The mixture was warmed to r.t. over 1 h and stirred at r.t. for 2 h.

Water ( $\sim 2$  mL) was added, and the resulting mixture was added to 50 mL of 0.1 M HCl overlaid with 50 mL of pentanes. The organic layer was washed with 0.1 M HCl ( $2 \times 40$  mL) followed by 40 mL of water, and then dried ( $\text{Na}_2\text{SO}_4$ ). GC analysis (A2) showed major peaks at 2.9 min (26%, **10a**) and 13.8 min (47%, **9a**) and minor peaks including 5.3 min (4%). Under these conditions, the comparison samples of silane **10a** and siloxane **11a** had retention times of 2.9 and 5.4 min, respectively.

About 1 mL of  $\text{CDCl}_3$  was added to the ether solution. Most of the solvent was removed by fractional distillation

(to b.p. 42 °C). NMR yields were obtained of 94% for **10a**, and 103% for **9a**.

A similar experiment was carried out using 0.2725 g (0.87 mmol) of **7** and ~2.6 mmol of (allyl)Me<sub>2</sub>SiCl. GC analysis (B3) of the crude product showed peaks at 3.9 min (35%, **10a**) and 11.1 min (43%, **9a**). NMR yields were obtained of 97% for **10a** and 95% for **9a**. The sample was then concentrated and chromatographed (hexanes) to give 0.1257 g (68% yield) of silole **9a** as a white solid having <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC retention time identical to those of **9a** obtained above using Me<sub>2</sub>SiCl<sub>2</sub>.

#### 4.6. Treatment of 2,2'-dibromobiphenyl (**7**) with *t*-BuLi followed by benzyldimethylchlorosilane: benzyl as a leaving group

A solution of 0.2622 g (0.84 mmol) of 2,2'-dibromobiphenyl (**7**) in 5.6 mL of THF was cooled to -70 °C, and 2.40 mL (3.6 mmol) of *t*-BuLi (1.5 M in pentane) was added dropwise, and the resulting mixture was stirred at -75 to -60 °C for 1 h. Then 0.90 mL of a mixture of equal volumes of benzyldimethylchlorosilane and Et<sub>3</sub>N (~2.5 mmol of chlorosilane) was added. The mixture was warmed to r.t. over 45 min and stirred at r.t. for 1.5 h.

Then water (~2 mL) was added to the reaction mixture, and the resulting mixture was added to water and extracted with ether (2 × 20 mL). The combined extracts were dried (Na<sub>2</sub>SO<sub>4</sub>), and analyzed by GC (A4) and showed peaks at 2.7 min (11%), 4.8 min (60%, **9a**), and 6.1 min (22%, **10b**) with a few minor peaks including 8.1 min (3%). Under these conditions, authentic samples of silane **10b** and siloxane **11b** came at 6.0 and 8.1 min, respectively. The solution was concentrated, and placed under oil pump vacuum (0.15 mm, 1 h) to give 0.5152 g of a yellow oil. NMR yields were obtained of 40% for **10b**, and 100% for **9a**. GC/MS of the product showed the major peak at 10.4 min (MS corresponded to the dibenzosilole **9a** [28]), with a smaller peak at 11.1 min (MS corresponded to dibenzyldimethylsilane (**10b**) [23a]), and several minor peaks including 8.7 min (MS corresponded to biphenyl [28]).

In a similar experiment, NMR yields of 34% for **10b** and 81% for **9a** and were obtained. Pure samples of silole **9a** and silane **10b** were obtained after two chromatographies of the product from an analogous experiment. Each had <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra identical to those of the authentic samples prepared above.

#### 4.7. Treatment of 2,2'-dibromobiphenyl (**7**) with *t*-BuLi followed by phenyldimethylchlorosilane: phenyl as a leaving group

A solution of 0.2867 g (0.92 mmol) of 2,2'-dibromobiphenyl (**7**) in 6 mL of THF was cooled to -75 °C, and 2.65 mL (4.0 mmol) of *t*-BuLi (1.5 M in pentane) was added. The resulting mixture was stirred at -75 °C to -60 °C for 1 h. Then 0.90 mL of a mixture of equal volumes of phenyldimethylchlorosilane and Et<sub>3</sub>N (~2.7 mmol

of chlorosilane) was added. The mixture was warmed to r.t. over 40 min and stirred at r.t. for 1 h 15 min.

Water (about 2 mL) was added, and the mixture was stirred for 2 min. The mixture was added to 40 mL of water, the resulting mixture was extracted with ether (2 × 15 mL), and the combined extracts were dried (Na<sub>2</sub>SO<sub>4</sub>). GC analysis (A4) showed peaks at 3.9 min (31%, **10c**), 4.8 min (35%, **9a**), and 14.1 min (19%, **9b**), and several minor peaks including one at 5.2 min (3%). In addition, a large peak prior to 2.5 min (believed to be PhMe<sub>2</sub>Si-*t*-Bu) was observed. Under these conditions, silane **10c** and siloxane **11c** had retention times of 3.9 and 5.2 min, respectively.

The solution was concentrated, and placed under oil pump vacuum (0.1 mm, 0.5 h) to give 0.6098 g of yellow oil. NMR yields were obtained of 53% for **10c**, 66% for **9a**, and 32% for **9b**. The region between δ 0.27 and 0.9 in the <sup>1</sup>H NMR contained major peaks at δ 0.27 (PhMe<sub>2</sub>Si-*t*-Bu, 0.42 (**9a**), 0.55 (**10c**), and 0.88 (PhMe<sub>2</sub>Si-*t*-Bu) and a smaller peak at 0.73 (**9b**). The peak at 0.73 was assigned as **9b** based on the fact the presence of **9b** was indicated by the GC/MS (below), isolation of **9b** from an analogous reaction mixture in 71% GC purity (below), and the reported [10] NMR shift for MeSi in **9b** (δ 0.71 in CCl<sub>4</sub>).

GC/MS of the product showed major peaks at 9.8 min (MS corresponded to diphenyldimethylsilane (**10c**) [28]) and 10.4 min (MS corresponded to dibenzosilole **9a** [28]). In addition, there were two smaller peaks at 7.7 and 13.4 min. The peak at 7.7 min showed *m/z* 192 (3, M<sup>+</sup>), 135 (100, PhMe<sub>2</sub>Si<sup>+</sup>), 105 (5, PhSi<sup>+</sup>), and was assigned as phenyldimethyl-*tert*-butylsilane (presumably from excess *t*-BuLi and PhMe<sub>2</sub>SiCl). The peak at 13.4 min showed *m/z* 272 (48, M<sup>+</sup>) and 257 (100, M<sup>+</sup> - Me), and was assigned as 1-methyl-1-phenyldibenzosilole (**9b**) [10]. A number of very small peaks were present including one at 8.7 min which corresponded to biphenyl [28], and one at 10.6 min which corresponded to siloxane **11c** [28].

An analogous experiment was carried out using 0.3384 g (1.08 mmol) of **7** and ~2.6 mmol of PhMe<sub>2</sub>SiCl. GC analysis (B1) of the crude product showed two major peaks at 3.8 min (40%, **10c**) and 4.1 min (41%, **9a**), and a smaller peak at 8.5 min (8.1%, probably **9b**). Under these conditions, siloxane **11c** came at 4.3 min; none was visible. Chromatography followed by preparative GC gave pure samples of silole **9a** and silane **10c**. Silole **9a** was obtained as a white solid, and had <sup>1</sup>H and <sup>13</sup>C NMR and GC retention time identical to those of **9a** obtained above using Me<sub>2</sub>SiCl<sub>2</sub>. Diphenyldimethylsilane (**10c**) was obtained as a colorless oil having <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to those of the authentic sample of **10c**. The IR spectrum was consistent with the structure, and with the reported spectrum [24]. GC analysis (B1) showed a peak at 3.8 min (100%). In a similar experiment, NMR yields of 60% for **10c**, 72% for **9a**, and 20% for **9b** were obtained. Chromatography of the remaining product followed by Kugelrohr distillation (0.05 mm, 110–125 °C) gave a sample of silole **9b** [10] as a colorless oil. GC analysis (A4)

showed the major peak at 14.1 min (71%, **9b**) and a minor peak at 20.0 min (16%). GC/MS analysis showed peaks at 11.0 min (major, MS corresponded to **9b**, above) and 11.8 min (minor). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , referenced to  $\text{CH}_3\text{NO}_2$  at  $\delta$  4.24) showed a large singlet at  $\delta$  0.72 (MeSi) and multiplets at  $\delta$  7.1–7.9 (ring protons), as well as several small singlets between 0.08 and 0.56 (impurities); this includes the peaks reported (in  $\text{CCl}_4$ ) for **9b** (SiMe at  $\delta$  0.71) [10].

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