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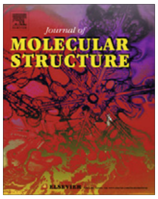

Synthesis and deprotonation of (phenylselenolatodimethylsilyl)bis(trimethylsilyl) methane: The crystal structure of $(Me_3Si)_2(Me_2SiBr)CH$

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ABSTRACT

The moisture-sensitive compound [{bromodimethylsilyl}bis(trimethylsilyl)methane], $[(Me_3Si)_2(Me_2SiBr)CH]$ **1** has been synthesized by the bromination of the hydride $[(Me_3Si)_2(Me_2SiH)CH]$ in CCl_4 in good yield. Compound **1** has been characterized by multinuclear NMR and a single crystal X-ray diffraction studies. The average Si–C and $BrMe_2Si$–C distances are, respectively, 1.894(2) and 1.886(2) Å. The Si–C–Si angle is 114.98(13)°. Treatment of **1** with NaSePh (obtained from the sodium triethylborohydride reduction of diphenyldiselenide) in benzene at room temperature resulted in the isolation of light yellow oil, [{phenylselenatodimethylsilyl}bis(trimethylsilyl)methane], $[(Me_3Si)_2(Me_2SiSePh)CH]$ **2**. Compound **2** has been metallated with methyllithium as well as lithium diisopropylamide (LDA) in THF to give $[(Me_3Si)_2(Me_2SiSePh)CLi{\cdot}2THF]$ **3**. Compounds **2** and **3** have been characterized by elemental analysis, mass and multinuclear NMR studies.

1. Introduction

There is considerable interest in the structures of simple compounds in which two or three bulky groups are attached to a central carbon atom, as for example, in $(Me_3C)_2CH_2$ [1], $(Me_3C)_3CH$ [2], $(Me_3Si)_2CH_2$ [3], $(Me_3Si)_3CH$ [4,5], $(Me_3Si)_3CBr$ [6], $(Me_2SiOMe)_3CBr$ [7] and $[(Me_2SiBr)_3CH]$, all of which were studied by electron diffraction but $[(Me_2SiBr)_3CH]$ by X-ray diffraction as well [8]. It therefore seemed to us appropriate to determine the structure of the related species $[(Me_3Si)_2(Me_2SiBr)CH]$, which as a solid could be studied by X-ray diffraction. A second aspect is that in recent years we have witnessed an increasing interest in the chemistry of bulky silyl-substituted ligands containing donor groups [9–11]. A series of organometallic compounds of the general type $MC(SiMe_3)_n(SiMe_2X)_{3-n}$ (X = OMe, NMe_2, or CH_2PPh_2, M = alkali metal or, for X = NMe_2, M = MgI), in which the organosilyl ligand is bound to the metal through both the central carbanionic site and the lone pairs of the group X, has been isolated. These compounds adopt a range of molecular or chain structures. For example, $LiC(SiMe_2CH_2PPh_2)_3$ is monomeric with strong M–C bond [12], $MgIC(SiMe_2NMe_2)_3$ [13] also monomeric with no normal M–C bond, $[LiC(SiMe_2OMe)_3]_2$ a dimeric [14] whereas $[LiC(SiMe_2NMe_2)_3]_\infty$ [15] or $[KC(SiMe_2NMe_2)_3]_\infty$ [16] are polymeric. We have previously reported the synthesis of tris{(diphenylphosphino)dimethylsilyl}methane, $HC(SiMe_2PPh_2)_3$ [17–19] and its sodium and potassium derivatives of the type, $(Ph_2PMe_2Si)_3CM$, (M = Na or K), by the metallation of tris{(diphenylphosphino)dimethylsilyl}methane $(Ph_2PMe_2Si)_3CH$, with MeM (M = Na or K) in THF or Et_2O. The lithium compound, $[Li(tmen)_2][C(SiMe_2PPh_2)_3]$(tmen = N,N,N′,N′-tetramethylethane-1,2-diamine) has been shown to crystallize in a lattice containing separated $[Li(tmen)_2]$ cations and planar $[C(SiMe_2PPh_2)_3]$ carbanions [17,18]. However, few derivatives of bulky silyl ligands containing chalcogen donors have been isolated [20]. In the present study we report the synthesis, structure and spectroscopic properties of $[(Me_3Si)_2(Me_2SiBr)CH]$ (**1**), $[(Me_3Si)_2\ (Me_2SiSePh)CH]$ (**2**) and its lithium derivative, $[(Me_3Si)_2(Me_2SiSePh)\ CLi{\cdot}2THF]$ (**3**).

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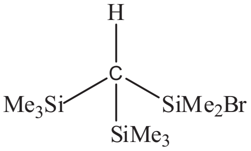

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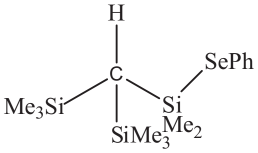

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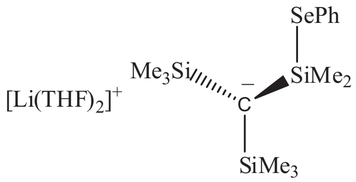

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2. Experimental

2.1. General

All reactions were conducted under an argon atmosphere and compounds were manipulated on a double-manifold vacuum line by the use of standard Schlenk techniques. Solvents were dried and distilled over sodium-potassium alloy (benzene, heptane) or sodium-benzophenone (Et_2O, THF) and stored over a K or Na mirror under argon. Microanalyses were carried out at Medac Ltd. (Brunel University) as well as University of North London. The EI mass spectra were recorded at 70 eV on a VG Autospec mass spectrometer. The NMR spectra were recorded at ambient temperature in C_6D_6 at 300.1 (^1H), 125.8 (^{13}C), 99.4 (^{29}Si) and 95.3 (^{77}Se) MHz and calibrated internally to residual solvent resonances, (^1H and ^{13}C), external $SiMe_4$ or Me_2Se. The quaternary carbon and ^{29}Si signals were detected by the INEPT (insensitive nuclei enhancement by polarization transfer) pulse technique. The compounds $CHBr_3$, Me_3SiCl, $[\{(CH_3)_2CH\}_2NH]$ (diisopropylamine), MeLi (1.4 M solution in diethyl ether) and BuLi (2.5 M solution in hexane) and Ph_2Se_2 were purchased from Aldrich and used as received. The compounds $(Me_3Si)_2CHBr$, $(Me_3Si)_2(Me_2SiH)CH$ [21] and lithium diisopropylamide (LDA) [22] were prepared as described in the literature.

2.2. Preparation of $[(Me_3Si)_2(Me_2SiBr)CH]$ **1**

A solution of Br_2 (12.15 g, 0.076 mol in CCl_4 (50 cm^3)) was added dropwise during 1 h to a solution of $[HC(SiMe_3)_2(SiMe_2H)]$ [21] (16.70 g, 0.076 mol) in CCl_4 (30 cm^3) at 0 °C, and the resulting orange solution was stirred at room temperature for 18 h. The solvent was removed and the orange residue distilled (b.p. 54 °C/ 10^{-3}) to give a colorless oil that crystallized on standing, m.p. 42 °C. Yield: 16.7 g (75%). Anal. Calc. for $C_9H_{25}BrSi_3$ (%): C, 36.34; H, 8.47; Found: C, 36.65; H, 8.60. MS: *m/z* (%): 281(100%) $[M{-}Me]^+$, 217(88%) $[M{-}Br]^+$, 203(15%) $[M{-}Br{-}CH_2]^+$, 129(75%) $[M{-}Br{-}CH_2{-}H{-}SiMe_3]^+$, 73(45%) $[SiMe_3]$, 59(14%) $[SiMe_2H]$, 45(7%) $[SiMe_2H{-}CH_2]^+$. IR (Nujol, CsBr plates) (cm^{-1}): 1251 m, δ(C–H); 1030 w; 845 vs, 730 w $\rho(CH_3)(Si)$; 670 w, ν_{as} (SiC); 610 vw, ν_s (SiC); 429 s, ν (Si–Br). ^1H NMR (300 MHz, C_6D_6): δ – 0.37 (1H, s, CH), 0.15 (18H, s, $SiMe_3$), 0.54 (6H, s, $SiMe_2$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 8.2 (Si_3C, $^1J(^{13}C_{methine}{-}^1H)$ 100.11 Hz), 3.16 ($SiMe_3$, $^1J(^{13}C_{methyl}{-}^1H)$ 118.78 Hz), 7.82 ($SiMe_2$), ^1J $(^{13}C_{methyl}{-}^1H)$ 121.29 Hz). $^{29}Si\{^1H\}$ NMR (300 MHz, C_6D_6): δ – 0.4 ($SiMe_3$); 24.7 ($SiMe_2Br$).

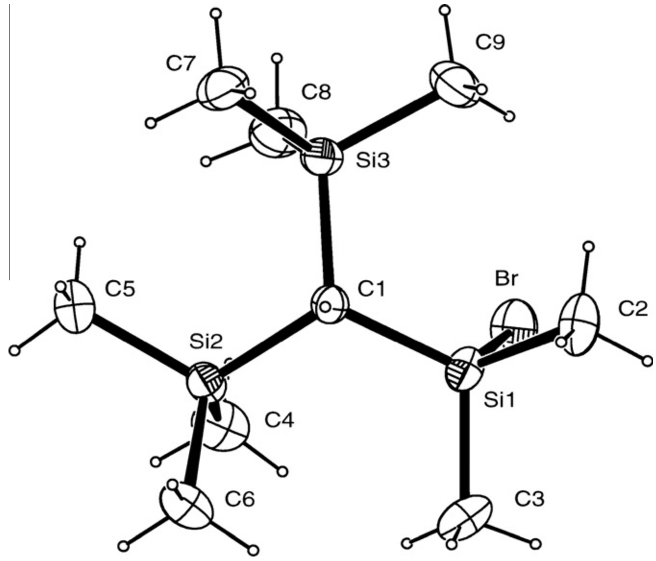


Fig. 2. The molecular structure of the compound **1**.

2.3. Preparation of $[(Me_3Si)_2(Me_2SiSePh)CH]$ (**2**)

Diphenyl diselenide (1.56 g, 4.9 mmol) was dissolved in diethyl ether (60 cm^3), and sodium triethylborohydride (10 cm^3 of a 1.0 M solution in THF, 10 mmol) was added by syringe. The yellow solution color disappeared within seconds. The colorless solution was

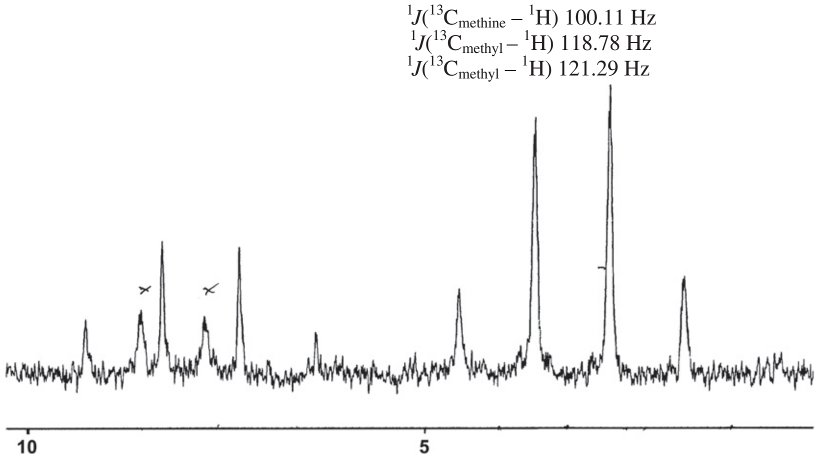


Fig. 1. ^{13}C (proton coupled) NMR Spectrum of $[(Me_3Si)_2(Me_2SiBr)CH]$ (**1**).

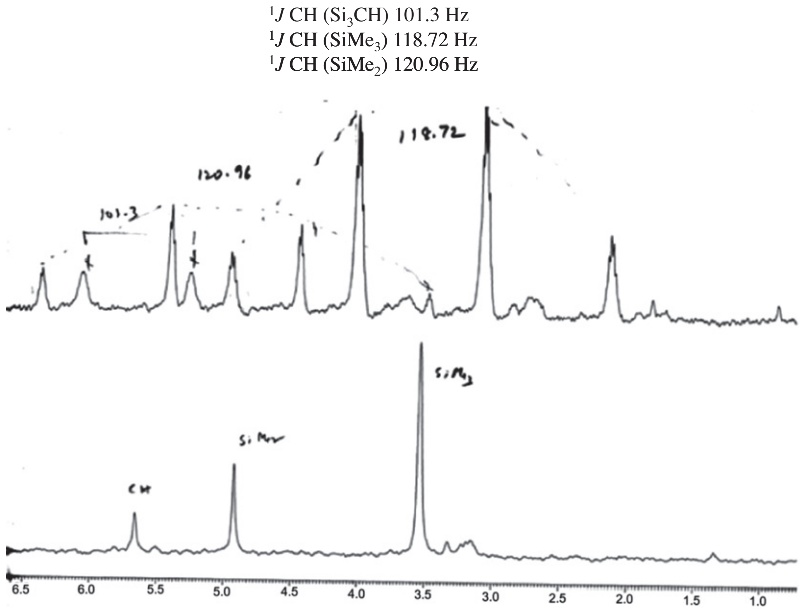

^1J CH (Si_3CH) 101.3 Hz
^1J CH ($SiMe_3$) 118.72 Hz
^1J CH ($SiMe_2$) 120.96 Hz

Fig. 3. ^{13}C NMR (proton coupled) spectrum of $[(Me_3Si)_2(Me_2SiSePh)CH]$ **2**.

stirred for 30 min and taken to dryness to give a white solid [23]. To the benzene suspension of NaSePh (1.32 g, 7.40 mmol) was added dropwise through a cannula a benzene solution of $[(SiMe_3)_2(SiMe_2Br)CH]$ (2.0 g, 6.75 mmol) and the mixture was stirred overnight. The solvent was removed completely in an external trap and the residue extracted with hexane. The solution was filtered to remove NaBr and the solvent stripped off under reduced pressure to give a light yellow oil. Yield: 3.3 g (80%). Anal. Calc. for $C_{15}H_{30}Si_3Se$(%): C, 48.22; H, 8.09; Found: C, 48.01; H, 7.84. MS: *m/z* (%): 374(10%) $[M]^+$, 359(50%) $[M{-}Me]^+$, 282(20%) $[M{-}Me{-}Ph]^+$, 217(85%) $[M{-}SePh]^+$, 201(15%) $[M{-}SePh{-}CH_4]^+$, 187(7%) $[M{-}SePh{-}CH_4{-}CH_2]^+$, 129(100%) $[M{-}SePh{-}CH_4{-}CH_2{-}SiMe_2]^+$, 73(75%) $[SiMe_3]$, 59(20%) $[SiMe_2H]$, 45(10%) $[SiMe_2H{-}CH_2]$. ^1H NMR (300 MHz, C_6D_6): δ −0.38 (1H, s, CH), 0.19 (18H, s $SiMe_3$), 0.38 (6H, s, $SiMe_2$), 7.57 (2H, d, Ph, *J*(HH) 8 Hz), 6.95 (3H, d, Ph, *J*(HH) 8 Hz). $^{13}C\{^1H\}$ NMR (300 MHz): δ 3.5 ($SiMe_3$), 4.9 ($SiMe_2$), 5.6 (CH), 126.83 (*p*-C), 127.5 (*m*-C), 129.0 (*o*-C), 137.4 (*i*-C). $^{29}Si\{^1H\}$ NMR (300 MHz, C_6D_6): – 0.3 ($SiMe_3$), 13.7 ($SiMe_2$), $^1J(^{29}Si^{77}Se)$ 108.4 Hz. $^{77}Se\ \{^1H\}$ NMR (300 MHz, C_6D_6): 112.3 (SePh).

2.4. Synthesis of $(Me_3Si)_2(Me_2SiSePh)CLi{\cdot}2THF$ (**3**)

2.4.1. Method A

A solution of $LiNPr^i_2$ (lithium diisopropylamide, LDA) was cooled to −78 °C and the compound $[(Me_3Si)_2(Me_2SiSePh)CH]$ (0.9 g, 3.35 mmol) added slowly. The mixture was stirred for 1 h at −78 °C, then brought to room temperature and the solvent was pumped away to leave a pale yellow sticky residue which was extracted with hexane. Removal of solvent from the extract gave a yellow solid. Yield: 0.8 g (90%), m.p. 103 °C.

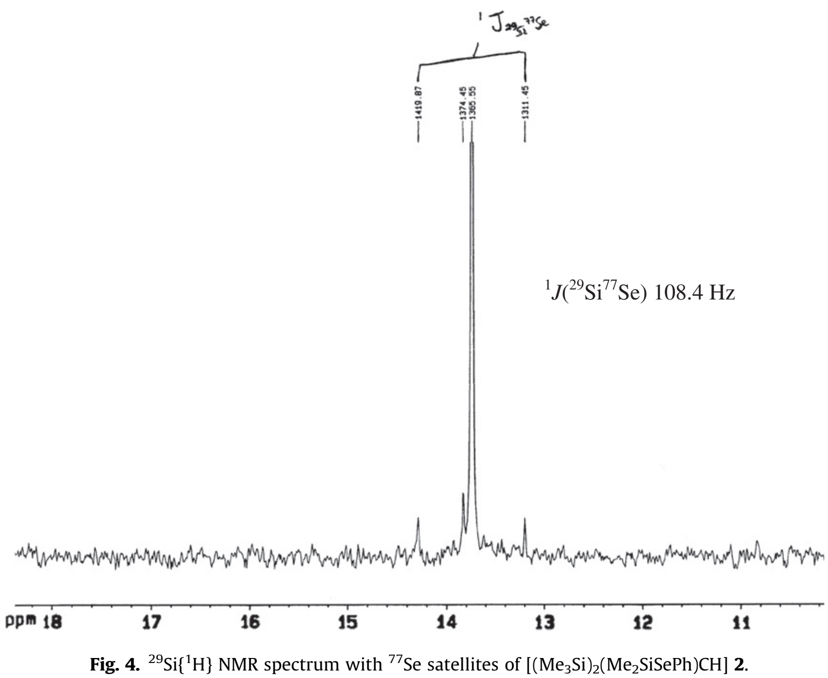

$^1J(^{29}Si^{77}Se)$ 108.4 Hz

Fig. 4. $^{29}Si\{^1H\}$ NMR spectrum with ^{77}Se satellites of $[(Me_3Si)_2(Me_2SiSePh)CH]$ **2**.

Table 1
Crystal data and structure refinement for compound **1**.

Empirical formula	$C_9H_{25}BrSi_3$
Formula weight	297.47
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$(No. 14)
Unit cell dimensions	a = 8.8476(4) Å α = 90° b = 14.8285(9) Å β = 104.038(3) c = 12.2137(5) Å γ = 90°
Volume	1554.5(1) $Å^3$
Z	4
Density (calculated)	1.27 Mg/m^3
Absorption coefficient	2.84 mm^{-1}
F(000)	624
Crystal size	0.4 × 0.2 × 0.2 mm^3
Theta range for data collection	3.76–27.90°
Index ranges	$-11 \leqslant h \leqslant 11$, $-19 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 16$
Reflections collected	9035
Independent reflections	3685 [R(int) = 0.050]
Reflections with $I > 2$sigma(I)	2994
Completeness to theta = 27.90°	99.2%
Tmax. and Tmin.	0.507 and 0.428
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3685/1/121
Goodness-of-fit on F^2	1.066
Final R indices [$I > 2$sigma(I)]	$R1$ = 0.044, w$R2$ = 0.097
R indices (all data)	$R1$ = 0.060, w$R2$ = 0.105
Largest diff. peak and hole	0.63 and −0.48 e $Å^3$

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

Si(1)–C(2)	1.863(3)
Si(1)–C(3)	1.863(3)
Si(i)–C(1)	1.869(2)
Si(1)–Br	2.2426(8)
Si(2)–C(6)	1.874(3)
Si(2)–C(5)	1.874(3)
Si(2)–C(1)	1.894(2)
Si(2)–C(4)	2.001(2)
Si(3)–C(7)	1.866(3)
Si(3)–C(9)	1.881(3)
Si(3)–C(1)	1.895(3)
Si(3)–C(8)	2.0252(17)
C(2)–Si(1)–C(3)	106.92(16)
C(2)–Si(1)–C(1)	113.06(13)
C(3)–Si(1)–C(1)	115.42(13)
C(2)–Si(1)–Br	106.67(10)
C(3)–Si(1)–Br	104.70(11)
C(1)–Si(1)–Br	109.40(8)
C(6)–SiC(2)–C(5)	105.09(15)
C(6)–Si(2)–C(1)	110.64(12)
C(5)–Si(2)–C(1)	112.87(13)
C(6)–Si(2)–C(4)	109.61(12)
C(5)–Si(2)–C(4)	106.78(13)
C(1)–Si(2)–C(4)	111.57(10)
C(7)–Si(3)–C(9)	105.53(14)
C(7)–Si(3)–C(1)	109.76(12)
C(9)–Si(3)–C(1)	113.96(13)
C(7)–SiC3)–C(8)	110.36(11)
C(9)–Si(3)–C(8)	105.19(12)
C(1)–Si(3)–C(8)	111.78(9)
Si(1)–C(1)–Si(2)	114.70(13)
Si(1)–C(1)–Si(3)	115.68(12)
SiC2)–C(1)–Si(3)	114.57(13)

2.4.2. Method B

A solution of MeLi (1.6 mmol) in THF (15 cm^3) was added at room temperature to a stirred solution of $[(Me_3Si)_2(Me_2SiSePh)CH]$ (0.59 g, 1.6 mmol) in THF (15 cm^3). Gas was evolved immediately. The resulting yellow solution was stirred for 4 h and the solvent removed to leave a sticky pale yellow solid which was extracted into hexane (20 cm^3). The filtered extract was reduced to 5 cm^3 and kept at −20 °C to give yellow crystals. Yield: 0.5 g (80%), m.p. 102 °C (dec.). Anal.Calcd. for $C_{15}H_{29}Si_3SeLi{\cdot}2C_4H_8O$ (%): C, 52.74; H, 8.65; Found: C, 48.14; H, 7.74. ^1H NMR (300 MHz, C_6D_6): δ 0.21 (18H, s, $SiMe_3$), 0.55 (6H, s, $SiMe_2$), 1.40 (8H, m, THF), 3.61 (8H, m, THF), 7.15–8.03 (5H, m, Ph). $^{29}Si\{^1H\}$ NMR (300 MHz, C_6D_6): −10.0 ($SiMe_3$), −0.5 ($SiMe_2$).

2.5. X-ray structure determination

Colorless crystals were obtained using vacuum sublimation at 65 °C. Crystallographic data for **1** were collected on a Nonius-Kappa CCD diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 1. Absorption corrections were applied using MULTISCAN. The structure was solved and refined using SHELXL-97 [24] as incorporated in the program package WINGX. The non-hydrogen atoms were refined anisotropically with hydrogen atoms in the riding mode. The ORTEP-3 programme [25] was used to prepare the molecular drawings. Selected bond lengths and angles for **1** are listed in Table 2.

3. Results and discussion

3.1. Synthesis and properties of $[(Me_3Si)_2(Me_2SiBr)CH]$ (1)

The compound bromodimethylsilylbis(trimethylsilyl)methane, $[(Me_3Si)_2Me_2\text{–}SiBr)CH]$ **1** has been synthesized by the bromination of the hydride $(Me_3Si)_2(Me_2\text{–}SiH)CH$ (prepared from the literature method [21]) in CCl_4 in good yield (Scheme 1). The compound **1** is readily isolated as colorless crystalline solid by removing the solvent under reduced pressure. It is soluble in hydrocarbon solvents. Elemental analysis agreed well with the above formulation.

The compound **1** is moisture-sensitive and is easily hydrolyzed.

3.1.1. Mass spectrum

The EI mass spectrum of **1** did not exhibit the molecular ion peak at m/z 296 $[M]^+$ but it showed a peak at m/z 281 (100%) due to the loss of one CH_3 from the molecular ion. The peak at m/z 217 corresponds to $[M\text{–}Br]^+$. The isotopic pattern and intensity of each of the peaks confirm the presence of one bromine. Other important fragments which could be identified are m/z(%): 203(15%) $[M\text{–}Br\text{–}CH_2]^+$, 129(75%) $[M\text{–}Br\text{–}CH_2\text{–}H\text{–}SiMe_3]^+$, 73(45%) $[SiMe_3]$, 59(14%) $[SiMe_2H]$, 45(7%) $[SiMe_2H\text{–}CH_2]^+$. Calculated and observed isotopic patterns for $C_8H_{22}BrSi_3$ $[M\text{–}Me]^+$ are in good agreement.

3.1.2. IR spectra

The IR spectrum of compound **1** shows medium intensity band at 1251 cm^{-1}, assignable to bending methyl vibrations, δ (CH_3). The bands at 1030, 845 and 730 cm^{-1} are assigned to methyl-silicon rocking modes ($\rho(CH_3)(Si)$). The silicon–carbon (tertiary) asymmetric and symmetric stretching vibrations (ν_{as}(SiC) and ν_s(SiC)) are observed at 670 and 610 cm^{-1} respectively. The strong band at 429 cm^{-1} is assigned to Si–Br stretching vibrations. These assignments are in good agreement with data from related bulky silyl substituted compounds [26–28].

3.1.3. ^1H NMR

The ^1H NMR spectrum of compound **1** recorded in C_6D_6 at 300 MHz showed signals at δ – 0.37 assigned to the methine proton. Other peaks at δ 0.15 and δ 0.54 are assigned to the $SiMe_3$ and $SiMe_2$ protons respectively.

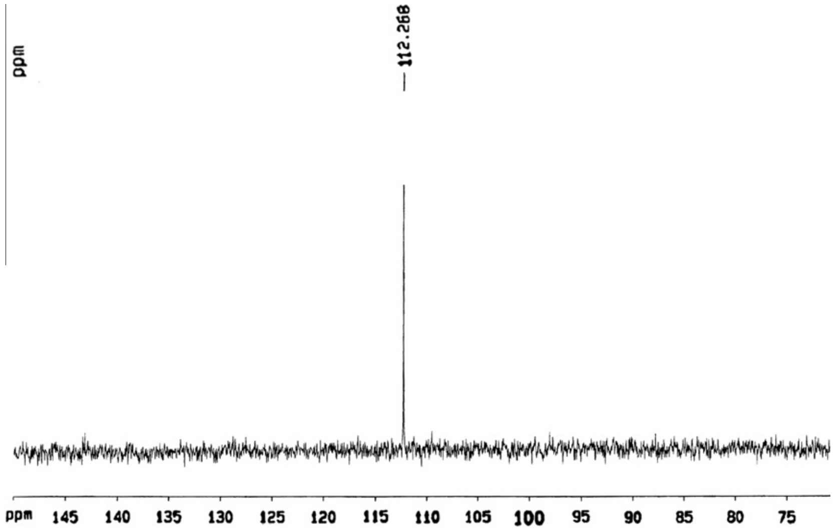
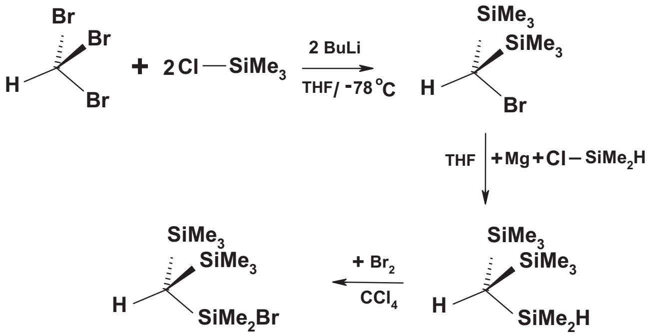
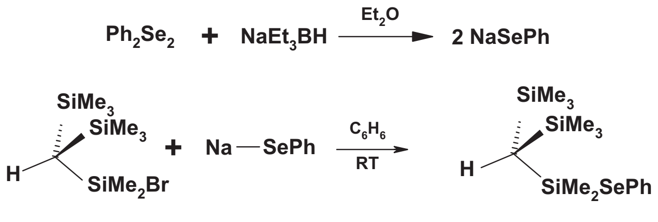


Fig. 5. ^{77}Se{^{1}H} NMR spectrum of [($Me_3Si)_2(Me_2SiSePh)CH$] **2**.



Scheme 1.



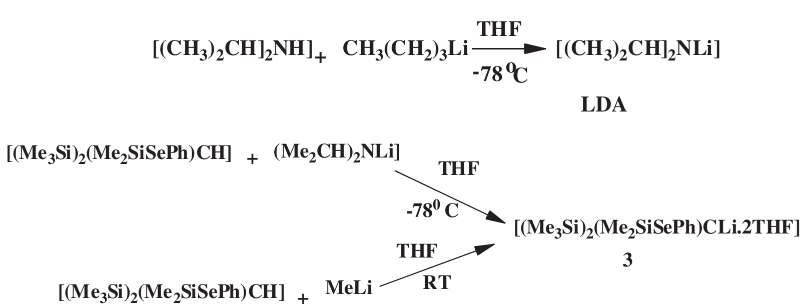
Scheme 2.

3.1.4. ^{13}C NMR

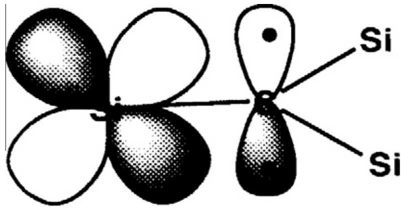
The proton decoupled ^{13}CNMR spectrum of compound **1** recorded in C_6D_6 solution at 300 MHz showed signals at δ 8.2 for the methine carbon. The signals at δ 3.2 and 7.8 are assignable to the $SiMe_3$ and $SiMe_2$ carbons respectively.

The spin–spin coupling of two magnetically active nuclei in neighboring atoms is thought to occur by ‘knock-on’ couplings from nucleus A to the near bonding electron 1 and from bonding electron 2 to nucleus B. Obviously, the efficiency of this coupling depends sharply on the probability of finding the bonding electrons at the nuclei. In MO theory, this probability is non-zero for s-type orbitals and their hybrids. Pure p-type orbitals, however, have no amplitude at the nucleus. From this argument, it follows that the coupling constant between a given pair of nuclei increases with the s-character of the bond between atoms.

The C–H bonds in SiMe groups are expected to be fairly normal sp^3 bonds since they are very nearly tetrahedrally arranged, as shown in numerous crystal structures. The magnitude of the coupling constant indicates an appreciable s-character; in a perfect sp^3 orbital, it is 25%. The tertiary C–H bonds, on the other hand, show lower coupling constants. To a first approximation, these bonds also are sp^3. The other three bonds in the system are C–Si bonds, though, and these three seem to absorb most of the s-character, leaving a very p-like orbital for the C–H. The p-orbital on the carbon atom is well positioned to overlap with empty orbitals of π symmetry on the silicon atoms (**I**).



Scheme 3.



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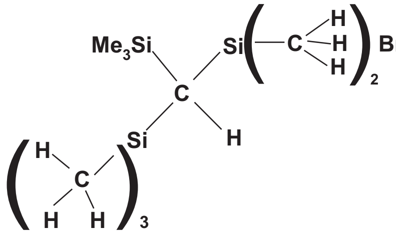
These effects could be at least partially steric in nature: the $SiMe_3$ groups, in repelling each other, will open the Si–C–Si bond angle up. The resulting geometry may be the main factor imposing the unusual hybridization of the central carbon. In organometallic compounds of trisyl-like ligands, the p-orbital carries even more electron density and so the s-character of the three Si–C bonds goes up even further as the limiting case of an sp^2 carbanion is approached.

In the proton-coupled ^{13}C spectrum (Fig. 1, **II**) various coupling constants are measured as follows: $^1J(^{13}C_{methine}–^1H)$ 100.11 Hz, $^1J(^{13}C_{methyl}–^1H)$ for $SiMe_3$ 118.78 Hz and that of $^1J(^{13}C_{methyl}–^1H)$ for $SiMe_2$ 121.29 Hz.



II

It is well known that the presence of electronegative groups increases the magnitude of the chemical shifts and C–H coupling constants [29]. In this case it can be seen that substituting the H by Br in **1** increases the chemical shift from 1.9 to 8.2 for the methine carbon, 2.4 to 3.2 for the $SiMe_3$ carbon and −0.6 to 7.8 for the $SiMe_2$ carbon. The coupling constants also increase in the order: ^1JCH ($SiMe_2$) from 120.0 Hz to 121.29 Hz, while the ^1JCH (Si_3C) increases from 98.0 Hz to 100.11 Hz. Although these increases are only small, they nonetheless demonstrate the effect of electronegative groups on the geometry of the central carbon.

3.1.5. $^{29}Si\{^1H\}$ NMR

The proton-decoupled $^{29}Si\{^1H\}$ NMR spectrum of compound **1** recorded in C_6D_6 solution at 300 MHz showed resonance at δ −0.4 assigned to the $SiMe_3$ silicon and δ 24.7 for the $SiMe_2$ silicon. The $SiMe_3$ silicon signal is at lower frequency than that of the hydride (δ 0.3) whereas the $SiMe_2$ silicon signal is at higher frequency than that in the hydride (δ −15.6).

The values of 0.1 ppm for the Si_3CH carbon and 6.3 ppm for the $SiMe_2Br$ silicon, given in a previous paper [30], are incorrect.

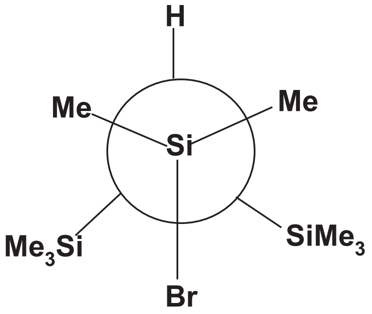
3.1.6. Crystal structure of $(Me_3Si)_2(Me_2SiBr)CH$

An ORTEP view of the bromide **1** with the atom numbering scheme is shown in Fig. 2. Crystallographic details are presented in Table 1 and bond lengths and angles are given in Table 2. The Br atom is disordered 78:9:13% over the three sides labeled Br, C(4) and C(8). The overlapping Br/C atoms sited were not resolved and were refined with partial occupancies. Bond lengths involving the disordered sites are unreliable.

The Si–C–Si bond angles are widened from the tetrahedral value to an average of 114.98(13)°, not significantly different from that observed in $[CH(SiMe_2Br)_3]$ {mean 115.16(3)°} [8]. The mean Si–C1 bond length to the central carbon {1.886(2) Å} is essentially identical with that in $[CH(SiMe_2Br)_3]$ {mean 1.884(5) Å}. The $BrMe_2Si$–C1 distance {1.869(2) Å} appears to be significantly shorter than the Me_3Si–C1 distance {1.894(2) Å}. The Si–Br bond length, 2.243(8) Å, is essentially similar to that, 2.256(2) Å, in $[CH(SiMe_2Br)_3]$ but is significantly longer than those in Br_nSiH_{4-n} and Me_nSiBr_{4-n} (2.14–2.235 Å) [31,32] and 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (2.197 Å) [33]. Further it is a little shorter than those [2.284(5), 2.283(1) Å] in two sterically encumbered polysilanes [34,35].

The flatter carbon is observed in all Si_3CH compounds. The sum of the three Si–C(1)–Si bonds are 345° whereas a similar total for a normal tetrahedral center would be 327°. The C–Si–C–Si torsion angles *ca.* −160°, 41° and 79° are similar to those in related compounds [8].

The Newman projection of the compound **1** is shown below.



Newman Projection

The analytical, spectral and crystal structure data suggest that the bromodimethylsilylbis(trimethylsilyl)methane has the distorted tetrahedral structure with the bromine atom away from the central carbon atom and silicon atom retains their tetrahedral configuration.

3.2. Synthesis and properties of $[(Me_3Si)_2(Me_2SiSePh)CH]$ (**2**)

The compound [{phenylselenatodimethylsilyl}bis(trimethylsilyl)methane], $[(Me_3Si)_2(Me_2SiSePh)CH]$ **2** has been synthesized by the reaction of sodium phenyl selenolate, NaSePh (obtained from the triethylborohydride reduction of diphenyl diselenide, Ph_2Se_2) with the bromide, $[(SiMe_3)_2(SiMe_2Br)CH]$ in benzene at room temperature in good yield (Scheme 2). The compound **2** is readily isolated as light yellow oil under reduced pressure. It is soluble in hydrocarbon solvents. Elemental analysis agreed well with the above formulation.

3.2.1. Mass spectrum

The EI mass spectrum of **2** exhibits the molecular ion peak at *m*/*z* 374 $[M]^+$. The peaks at *m*/*z* 359, 282 and 217 are due to the rapid loss of CH_3, Ph and SePh fragments respectively from the molecular ion peak $[M]^+$. The isotopic pattern and intensity of the peaks confirm the presence of one selenium atom. Other important fragments which could be identified are: MS: *m*/*z*(%): 201(15%) $[M–SePh–CH_4]^+$, 187(7%) $[M–SePh–CH_4–CH_2]^+$, 129 (100%) $[M–SePh–CH_4–CH_2–SiMe_2]^+$, 73(75%) $[SiMe_3]$, 59(20%) $[SiMe_2H]$, 45(10%) $[SiMe_2H–CH_2]$. Calculated and observed isotopic pattern for $C_{15}H_{30}Si_3Se$ (M^+) are in good agreement.

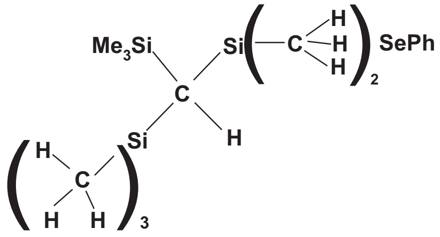
3.2.2. ^1H NMR

The ^{1}H NMR spectrum of compound **2** recorded in C_6D_6 at 300 MHz shows singlet signals at δ – 0.38, δ 0.19 and δ 0.38 assignable to the methine (CH), $SiMe_3$ and $SiMe_2$ protons respectively. The *ortho*- and *meta*- and *para*-phenyl protons appear as doublets at δ 7.57 and δ 6.95 respectively. The proton-proton coupling constants (*J* 8 Hz) are in the usual range.

3.2.3. ^{13}C NMR

The proton decoupled $^{13}C\{^1H\}$ NMR spectrum of compound **2** recorded in C_6D_6 solution at 300 MHz shows signals at δ 5.6 for the methine carbon. The signals at δ 3.5 and 4.9 are assignable to the $SiMe_3$ and $SiMe_2$ carbons respectively. The chemical shift values of compound **2** are similar to the values obtained for **1** and clearly indicate the replacement of bromide by weaker nucleophile SePh. The *ipso*-phenyl carbon appears as strong downfield shift at 137.4. The *ortho*-, *meta*- and *para*-phenyl carbon appear in their usual positions.

In the proton-coupled ^{13}C spectrum (Fig. 3, **III**) various coupling constants are calculated as follows: $^1J(^{13}C_{methine}–^1H)$ 101.3 Hz, $^1J(^{13}C_{methyl}–^1H)$ for $SiMe_3$ 118.72 Hz and that of $^1J(^{13}C_{methyl}–^1H)$ for $SiMe_2$ 120.96 Hz.



III

These coupling constants differ significantly from those of **1**.

3.2.4. $^{29}Si\{^1H\}$ NMR

The proton-decoupled $^{29}Si\{^1H\}$NMR spectrum of compound **2** (Fig. 4) recorded in C_6D_6 solution at 300 MHz shows resonances at δ – 0.3 assigned to the $SiMe_3$ silicon and δ 13.7 for the $SiMe_2$ silicon. There is a marked change in the chemical shift of $SiMe_2$ signal in compound **2** relative to compound **1**. The $SiMe_2$ silicon resonance in compound **2** is associated with ^{77}Se satellites (intensities 1:6:1, Fig. 4). The coupling constant $^1J(^{29}Si^{77}Se)$ 108.4 Hz is in good agreement with the reported values for other related compounds [36].

3.2.5. $^{77}Se\{^1H\}$ NMR

The $^{77}Se\{^1H\}$ NMR of compound **2** (Fig. 5) shows a single resonance at δ 112.3 ppm. The observed chemical shift is in good agreement with related selenium compounds [36]. The chemical shift of diphenyl diselenide is at δ 459.7 ppm. This indicates that the observed compound is free from diselenide impurity.

The analytical and multinuclear NMR data suggest that the phenylselenolatodimethylsilylbis(trimethylsilyl)methane has the distorted tetrahedral structure with the SePh group away from the central carbon atom and silicon atom retains their tetrahedral configuration.

3.3. Synthesis and properties of $[(Me_3Si)_2(Me_2SiSePh)CLi\cdot 2THF]$ (**3**)

The new bulky ligand $[(Me_3Si)_2(Me_2SiSePh)CH]$ has been metallated with methyllithium as well as lithium diisopropylamide (LDA) in THF. Using LDA instead of MeLi essentially makes the deprotonation steps unambiguous, no lithium–halogen exchange is possible in this case [22,37] (Scheme 3).

The lithiation has been completed within 2 h at room temperature in contrast with that of the related substrate $(Me_3Si)_3CH$ which requires 4–6 h in refluxing THF [38]. The compound has been isolated as air- and moisture-sensitive pale yellow solid in good yield. It is soluble in pentane, hexane, benzene, toluene and THF. Carbon and hydrogen analyses are not satisfactory due to air- and moisture-sensitivity of the compound.

3.3.1. ^1H NMR

The ^{1}H NMR spectrum of lithium derivative shows peaks at δ 0.21 and 0.55 assignable to $SiMe_3$ and $SiMe_2$ and at 3.6 and 1.4 for complexed THF. The integration of the peaks suggests that there are two THF molecules coordinated to Li.

The absence of CH peak confirms the deprotonation. The observed chemical shifts for $SiMe_3$ and $SiMe_2$ protons are downfield compared to free ligand. The multiplets at 8.03 and 7.15 are assigned to phenyl protons.

3.3.2. $^{29}Si\{^1H\}$ NMR

The $^{29}Si\ \{^1H\}$ NMR spectrum shows two peaks at δ -10.0 and -0.5 ppm which are assigned to $SiMe_3$ and $SiMe_2$ silicon signals. The observed chemical shifts were shifted upfield to those in **2**. Similar ionic structures for lithium derivative have been reported earlier [17–19].

4. Conclusion

The present study involves synthesis and structure of bromodimethylsilylbis(trimethylsilyl)methane, $(Me_3Si)_2(Me_2SiBr)CH$, **1**. The bromide has been successfully converted into a bulky ligand, $(Me_3Si)_2(Me_2SiSePh)CH$, **2** with a potential selenium donor function. Compound **2** has been metallated with LDA as well as with MeLi. The NMR spectra closely resemble those of the previously characterized lithium derivatives, suggesting that $(Me_3Si)_2(Me_2SiBr)CLi\cdot 2THF$, **3**, exists as ion pairs in solution.

Investigations on the potential of **2** and **3** as ligand transfer reagents towards transition metal ions are in progress and will be reported later.

Supplementary material

CCDC 861028 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033).

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