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SOME TRIS(TRIMETHYLSILYL)METHYL DERIVATIVES OF BORON, ALUMINIUM AND GALLIUM *

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Summary

Some compounds containing the very bulky $(Me_3Si)_3C$ group (= Tsi) attached to boron have been prepared. Treatment of the fluoride TsiB(F)OR ($R = (CH_2)_4$Tsi) with $LiAlH_4$ in Et_2O followed by hydrolysis gave TsiB(OH)OR, and treatment of the same fluoride with $LiAlH_4$ in THF gave a compound thought to be $TsiBH_3Li \cdot 2THF$. This compound was very air-sensitive and thermally unstable, decomposing at 50°C to give TsiH. It reacted with MeOH to give $TsiB(OMe)_2$ and with catechol to give [2-tris(trimethylsilyl)methyl]-1,3,2-benzodioxaborole. The latter reacted with aqueous NaOH to give $TsiB(OH)_2$, and with MeLi in Et_2O to give $TsiBMe_2$, which was also obtained in a similar way from $TsiB(OMe)_2$. The compound $TsiAlCl_2$ was obtained in low yield from the reaction between TsiLi and $AlCl_3$ in Et_2O/THF. Hydrolysis of the remaining product mixture gave the alcohol $Tsi(CH_2)_4OH$, which was also made by methanolysis of $Tsi(CH_2)_4OSiMe_3$, itself made from TsiLi and $I(CH_2)_4OSiMe_3$. The alcohol underwent rearrangement to $(Me_3Si)_2CH(CH_2)_4$-$OSiMe_3$ on treatment with MeONa/MeOH. The compound TsiGa(OH)Me was isolated after treatment of $GaCl_3$ with TsiLi from which residual MeLi had not been removed.

Introduction

We recently described the preparations of the compounds TsiB(F)OR (I) and TsiB(Ph)OR, where Tsi denotes the very bulky tris(trimethylsilyl)methyl group, $(Me_3Si)_3C$ and $R = (CH_2)_4$Tsi [1]. We now describe the results of a study of compounds derived from reactions of I and present some preliminary data on tris(trimethylsilyl)methyl derivatives of aluminium and gallium. A new organosilicon

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June 1983. J.D.S. had the privilege of being a research student under the supervision of Professor Emeléus in 1955–1958.

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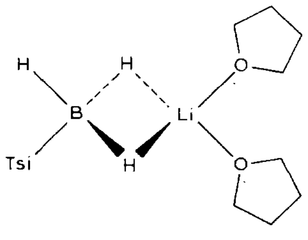
rearrangement is also described.

$TsiBF[O(CH_2)_4Tsi]$ (I) $TsiBH_3Li \cdot 2THF$ (II)

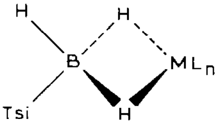
Results and discussion

An attempt was made to prepare the hydride TsiB(H)OR by treating I with $LiAlH_4$ in refluxing Et_2O. The ^1H NMR spectrum of a sample of the crude product in CCl_4 after separation from the excess of $LiAlH_4$ indicated that it was a mixture, possibly containing material produced by accidental hydrolysis. The product was treated with water to give, after work-up, the hydroxide TsiB(OH)OR in 72% yield. The elemental analysis, ^1H, ^{13}C and ^{11}B NMR spectra and the mass spectrum were consistent with this formulation.

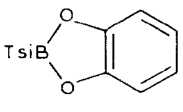
A different result was obtained when I was treated with $LiAlH_4$ in refluxing THF. Some of the product was isolated without hydrolysis as colourless needles, II, while the remainder was hydrolysed to give the hydroxide TsiB(OH)OR mentioned above. Compound II was very unstable in the air (because of this a reliable elemental analysis could not be obtained), and reacted with water with vigorous gas evolution. Although the mass spectrum clearly indicated the presence of some $TsiB(H)O(CH_2)_4Tsi$, the other spectroscopic characteristics of the solid were consistent with the formulation $TsiBH_3Li \cdot 2THF$. Thus the ^1H NMR spectrum showed only one peak in the Tsi region (indicating the loss of one of the Tsi groups, which was reasonably assumed to be that in the $O(CH_2)_4Tsi$ ligand) and the expected signals for THF, with the correct integration ratio. Both ^{11}B and ^{10}B NMR spectra showed a resonance on the high field side of $BF_3 \cdot Et_2O$ ($\delta(^{11}B) - 30.1$ ppm), consistent with an anionic four-coordinate boron centre [2]; at 35°C this resonance was split to give a well resolved 1/3/3/1 quartet, indicating the presence of three equivalent protons attached to boron. Compounds of the type $LiBR_nH_{4-n}$, usually obtained by treatment of BR_nF_{3-n} species with $LiAlH_4$, are well known [3].



(IIa)



(III)



(IV)

A reasonable structure for compound II is that shown as IIa; the high solubility in pentane is presumably attributable to the presence of the Tsi group. Similar structures have been suggested to account for the properties of lithium borohydride in donor solvents [4]. The ^{11}B NMR spectra show that at 35°C there is rapid exchange between bridging and terminal hydrogen atoms in IIa. At low temperatures, the lines of the quartet merge; the four peaks can still be distinguished at −60°C, but at −90°C there is only a broad singlet. There thus seems to be a slowing down of the exchange process, but the bridging and terminal hydrogens are not fully distinct on the NMR timescale at −90°C. Borohydrides with di-μ-H bridges are well known [5], as are mono μ-H and tri-μ-H-bonded derivatives. Exchange between bridging and terminal hydrogens in di-μ-H-bonded borohydrides (III) is normally rapid, but in a few cases it is sufficiently slow for the rate to be determined by NMR spectroscopy. Attempts are being made to determine the structure of II by X-ray diffraction, but these are hampered by the sensitivity of the compound to hydrolysis.

Compound II was also obtained by treatment of TsiB(OH)OR with $LiAlH_4$ in THF. It is thermally unstable, and when heated at 50°C it gave $(Me_3Si)_3CH$ in high yield. It reacted with MeOH to give $TsiB(OMe)_2$, and with catechol to give [2-tris(trimethylsilyl)methyl]-1,3,2-benzodioxaborole (IV). Unlike simple 2-alkyl-1,3,2-benzodioxaboroles [6], IV was not reduced by $LiAlH_4$, but like other 1,3,2-benzodioxaboroles [7] it could be hydrolysed to the corresponding boronic acid, $TsiB(OH)_2$ (V). It also reacted with MeLi in Et_2O to give $TsiBMe_2$, which was also obtained in a similar way from $TsiB(OMe)_2$.

Each of the tris(trimethylsilyl)methylboron compounds gave a well-defined ^{11}B NMR signal with a chemical shift in the range expected from data for analogous compounds [2] *. The $O(CH_2)_4Tsi$ group, like other alkoxy groups, is a strong electron donor towards boron, and shifts the signal to higher field compared with that from trialkylboranes. In mass spectra, ions containing boron could be recognised by their isotope patterns. The peak corresponding to loss of a Me group from the parent species was usually prominent, but the base peak was commonly that for Me_3Si^+. Compound IV and $TsiBMe_2$ gave strong peaks corresponding to $[(Me_3Si)_2CB]^+$ (confirmed by an accurate mass determination in the case of IV).

From the reaction between TsiLi and $AlCl_3$ (ca. 0.8/1 mol ratio) in Et_2O/THF the compound $TsiAlCl_2$ was isolated in low (15%) yield. The elemental analysis and the IR, ^1H NMR, and mass spectra were consistent with this formulation, and the molecular weight as determined by freezing point depression in cyclohexane was 321, compared with the 329 calculated for $TsiAlCl_2$. The apparently monomeric state of this compound in the gas phase and in solution is of interest, and is being further studied.

The product mixture from the above reaction after removal of the $TsiAlCl_2$ was treated with MeOH to give some TsiH and the alcohol $Tsi(CH_2)_4OH$ (the latter in 20% yield based on the TsiLi used). We think it likely that this alcohol (and possibly some, at least, of the TsiH) was produced by hydrolysis of $TsiAl(Cl)[O(CH_2)_4Tsi]$, the formation of which would parallel that of $TsiB(F)[O(CH_2)_4Tsi]$ from TsiLi and BF_3 in Et_2O/THF [1], but it could have come from hydrolysis of $LiO(CH_2)_4Tsi$ formed by reaction between TsiLi and THF. (The possible formation of this lithium alkoxide in the TsiLi/BF_3/THF reaction has been discussed [1].)

To confirm the identity of the alcohol it was synthesized independently by acid-catalysed methanolysis of $Tsi(CH_2)_4OSiMe_3$, itself produced by reaction of TsiLi with $I(CH_2)_4OSiMe_3$. When treated with MeOH containing NaOMe the alcohol underwent rearrangement to give $(Me_3Si)_2CH(CH_2)_4OSiMe_3$.

$$TsiLi + I(CH_2)_4OSiMe_3 \rightarrow Tsi(CH_2)_4OSiMe_3$$

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* The ^{11}B spectrum of TsiB(Ph)OR was incorrectly reported [1]. The ^{11}B chemical shift is 53.8 ppm.

$Tsi(CH_2)_4OSiMe_3 + MeOH\ (+H^+) \rightarrow Tsi(CH_2)_4OH$

$Tsi(CH_2)_4OH + MeOH/MeONa \rightarrow (Me_3Si)_2CH(CH_2)_4OSiMe_3$

This is apparently the first example of a 1,6-migration of silicon from carbon to oxygen, but the precisely analogous 1,4-rearrangement of $Tsi(CH_2)_2OH$ to give $(Me_3Si)_2CH(CH_2)_2OSiMe_3$ was recently reported [8], and there are many examples of 1,2- and 1,4-migrations of silicon from carbon to oxygen [9]. The 1,6-migration we have observed, like that of the analogous 1,4-process, is facilitated by stabilization of the forming carbanionic centre by the two remaining Me_3Si groups and by relief of steric strain [8].

A preliminary study was made of the reaction of $GaCl_3$ with TsiLi in Et_2O/THF but, residual MeLi not having been removed after formation of the TsiLi, the product isolated appeared to be TsiGa(OH)Me. The elemental analysis and the IR, ^1H NMR, and mass spectra were consistent with this formulation. Presumably $MeGaCl_2$ was first formed, then converted into TsiGa(Cl)Me, which underwent hydrolysis during work-up. Probably $TsiGaCl_2$ was also formed, but lost in the work-up.

Experimental

General

Reactions involving use of organolithium reagents, $LiAlH_4$, compound II, and other air-sensitive materials were carried out under Ar using Schlenk tube techniques. All solvents were carefully purified (where necessary) and dried by standard techniques.

Sublimations were carried out under vacuum, and the sublimate was tapped down into a Schlenk tube under Ar.

All compounds containing the Tsi group showed absorptions in the IR at 3020–2800, 1430–1380, 1305–1210, 910–800, and 700–660 cm^{-1}.

The NMR spectra of air-sensitive materials were determined with samples sealed in NMR tubes under Ar. The ^1H NMR spectra were recorded at 60 MHz on a Perkin–Elmer R12 spectrometer, usually in CCl_4 with CH_2Cl_2 as reference. The ^{11}B spectra were recorded at 25.7 MHz (in C_6D_6, relative to $BF_3 \cdot Et_2O$), and ^{13}C spectra at 20.15 MHz (relative to Me_4Si) on a Bruker multinuclear WP80 S4 FT spectrometer; negative shifts are to high field from the reference peak.

Mass spectra were recorded at 70 eV with an AEI MS30 spectrometer. The figures in parentheses after the m/e values are the percentage abundances relative to the base peak, which, unless otherwise indicated, was at m/e 73 ($[Me_3Si]^+$).

TsiB(F)OR (I). This was prepared as previously described [1].

Treatment of I with $LiAlH_4$ in Et_2O

A solution of I (1.0 g, 1.77 mmol) in Et_2O (20 cm^3) was added to $LiAlH_4$ (0.12 g, 3.1 mmol) in Et_2O (30 cm^3) under Ar at room temperature, and the mixture was refluxed for 3 h, then evaporated to dryness. The residue was extracted with pentane, and the pentane solution was evaporated to leave a solid with a ^1H NMR spectrum having overlapping peaks in the Me_3Si region and multiplets at δ 1.5–1.8 and 3.8 characteristic of $O(CH_2)_4$. The crude product (0.5 g) was treated with water, and this was followed by extraction with pentane. The pentane extracts were washed with water, dried ($MgSO_4$), and filtered, and the solvent was evaporated to leave hydroxy[tris(trimethylsilyl)methyl][5,5,5-tris(trimethylsilyl)pentoxy]borane TsiB(OH)[O(CH_2)$_4$Tsi], (0.37 g), m.p. 140°C (decomp.) (Found: C, 51.7; H, 10.9. $C_{24}H_{63}BO_2Si_6$ calcd.: C, 51.3; H, 11.2%); IR (KBr), ν(OH) 3680 (s, sharp), ν(BO) 1320 cm^{-1} (cf. ref. 10); ^1H NMR (CCl_4), δ 0.36 (s, 27H, Me_3Si), 0.43 (s, 27H, $SiMe_3$), 1.70 (br, m, 6H, CH_2), 4.0 (m, 2H, CH_2O); ^{13}C NMR, δ 3.1 (CH_3 of Tsi(CH_2)$_4$O), 4.5 (CH_3 of TsiB), 5.0, 5.2 (*C*($SiMe_3$)), 27.8 (CH_2), 31.7 (CH_2), 33.5 (CH_2), 63.1 (OCH_2); ^{11}B NMR, δ 29.6 ppm (s). The mass spectrum showed the expected prominent peak at *m/e* 547 (19) ($[M - Me]^+$), with additional peaks at 531 (4), 243 (24), 201 (16), 199 (17), 157 (19), and 125 (30).

Reaction of I with $LiAlH_4$ in THF

A solution of I (1.4 g, 2.5 mmol) in THF (10 cm^3) was added dropwise to $LiAlH_4$ (0.1 g, 2.6 mmol) in THF (20 cm^3) at room temperature under Ar. The mixture was subsequently boiled under reflux for 3 h, and the solvent then removed. The residue was extracted with pentane, and the pentane solution was kept at − 10°C to give II as colourless needles (0.29 g, 40%); (Found: C, 50.1; H, 11.2. $C_{18}H_{46}BLiO_2Si_3$ calcd.: C, 54.5; H, 11.6%). ^1H NMR δ (C_6H_6) 0.35 (s, 27H, Me_3Si), 1.42 (m, 8H), 3.47 (m, 8H); ^{11}B NMR −30.1 ppm (q, $J(^{11}B–H)$ 80, $J(^{10}B–H)$ 26.7 Hz). Off-resonance experiments with ^{10}B spectra showed that the signal from the B–H protons was under that from the protons of the Me_3Si group. The mass spectrum had prominent peaks at *m/e* 531 (17) ($[TsiB(H)O(CH_2)_4Tsi - Me]^+$), 331 (11) ($[TsiB(H)OSiMe_3 - H]^+$) and 317 (17) ($[TsiB(H)OSiMe_3 - Me]^+$), 243 (17) ($[TsiBO - Me]^+$), 229 (23) ($[TsiBH_2 - Me]^+$), 217 (64) ($[TsiH - Me]^+$), 170 (47) ($[(Me_3Si)_2CBH]^+$) and 155 (88) ($[(Me_3Si)_2CBH - Me]^+$) and the base peak at 73. A flame test indicated the presence of lithium.

The pentane mother liquor after removal of the needles of II was shaken with water, some light petroleum (b.p. 30–40°C) was added, and the organic layer was separated, washed with water, dried ($MgSO_4$) and evaporated, to give TsiB(OH)OR (0.5 g, 36%), with ^1H and ^{11}B NMR spectra identical to those of the sample described above.

Reactions of II

(a) A solution of II (0.10 g, 0.25 mmol) in CH_2Cl_2 (2 cm^3) was placed in a Schlenk tube which had been previously flushed with argon, and through which a stream of argon was passed. A solution of MeOH (0.275 g, 0.86 mmol) in CH_2Cl_2 was added dropwise at room temperature, and the mixture was stirred until hydrogen evolution ceased (ca. 0.5 h). The solvent was removed and the residue extracted with pentane. The solution was filtered, the pentane evaporated, and the residue sublimed (50°C/0.1 mmHg) to give dimethoxy[tris(trimethylsilyl)methyl]borane, $(Me_3Si)_3CB(OMe)_2$ (0.021 g, 28%), m.p. 150°C (decomp.) (Found: C, 47.4; H, 10.7. $C_{12}H_{33}BO_2Si_3$ calcd.: C, 47.4; H, 10.9%); ^1H NMR (CCl_4) δ 0.32 (s, 27H, Me_3Si), 3.62 (s, 6H, OCH_3); ^{11}B NMR, δ 31.0 ppm. The mass spectrum showed the expected peak at 289 (12) ($[M - Me]^+$), but it was complicated by the presence of peaks attributable to the hydrolysis product V; thus the base peak was at *m/e* 243 ($[(Me_3Si)_3CBO - Me]^+$), and there was a prominent peak at *m/e* 261 ($[V - Me]^+$).

(b) A solution of catechol (0.50 g, 0.45 mmol) in CH_2Cl_2 (3 cm^3) was added dropwise at room temperature to a solution of II (0.089 g, 0.20 mmol) in CH_2Cl_2 (2 cm^3) under Ar, and the mixture was stirred for 0.5 h. The solvent was removed and the residue extracted with pentane. The pentane solution was filtered, and evaporated to leave IV as a colourless solid (0.072 g, 92%), m.p. 42–43°C (Found: C, 54.5; H, 8.9. $C_{16}H_{31}BO_2Si_3$ calcd.: C, 54.8; H, 8.7%); IR (KBr), $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ 1470, ν(B–O) 1290, CH_{def} 740 cm^{-1}. ^1H NMR (CCl_4/CH_2Cl_2), δ 0.42 (s, 27H, Me_3Si), 7.02–7.11 (m, 4H, aryl-H); ^{11}B NMR, 34 ppm (br. s). The mass spectrum showed the molecular ion at *m/e* 350 (5), and the expected prominent peak at 335 (39) ($[M - Me]^+$); Found: 335.1480; Calcd. 335.1490); the base peak was at *m/e* 169 ($[(Me_3Si)_2CB]^+$; Found: 169.1046; Calcd. 169.1040).

Reaction of TsiB(OH)[O(CH$_2$)$_4$Tsi] with LiAlH$_4$

A solution of TsiB(OH)[O(CH_2)$_4$Tsi] (0.30 g, 0.53 mmol) in THF (3 cm^3) was added to $LiAlH_4$ (0.2 g) in THF (10 cm^3) and the mixture was heated under reflux for 5 h. The solvent was removed and the residue extracted with pentane. The pentane extract was filtered and kept at −10°C to give needles of II, which had a ^{11}B NMR spectrum identical with that of the sample described above.

Reaction of IV with aqueous NaOH

When aqueous NaOH (8 cm^3 of 0.12 *M* solution; 1 mmol) was added to a solution of IV (0.115 g, 0.33 mmol) in THF (2 cm^3) at room temperature a vigorous reaction took place. The mixture was kept overnight, then neutralized with dilute hydrochloric acid. Extraction with light petroleum (b.p. 30–40°C), followed by washing, drying ($MgSO_4$) and evaporation of the petroleum solution, gave a solid residue, which was sublimed (60°C/0.1 mmHg) and found to be dihydroxy[(trimethylsilyl)methyl]borane (V), (0.30 g, 33%); m.p. 56°C (decomp.) (Found: C, 43.89; H, 10.4. $C_{10}H_{29}BO_2Si_3$ calcd.: C, 43.5; H, 10.5%); IR (KBr), ν(O–H) 3660 and 3430 br, ν(B–O) 1350 cm^{-1}; ^1H NMR (CCl_4), δ 0.35 (s, 27H, Me_3Si), 4.20 (s, 2H, OH); ^{11}B NMR, δ 30.6 ppm. The mass spectrum showed the expected $[M - Me]^+$ ion at *m/e* 261 (21), with the base peak at *m/e* 243 ($[TsiBO - Me]^+$). This may indicate that the dihydroxyborane (boronic acid) (V) had been partly converted into the boroxine TsiBO in the probe of the instrument.

Reactions of IV

(a) A vigorous reaction took place when MeLi in Et_2O (1 cm^3 of 0.60 *M* solution) was added dropwise to a solution of IV (0.10 g, 0.29 mmol) in Et_2O (3 cm^3) under Ar at room temperature. The mixture was stirred for 4 h at room temperature, then the solvent was removed and the residue extracted with pentane. The pentane solution was filtered and evaporated, and the residue was sublimed (45°C/0.1 mmHg) to give dimethyl[tris(trimethylsilyl)methyl]borane, $TsiBMe_2$, (0.047 g, 60%), m.p. 80°C (decomp.) (Found: C, 53.5; H, 11.9. $C_{12}H_{33}BSi_3$ calcd.: C, 52.9; H, 12.2%); ^1H NMR (CCl_4), δ 0.26 (s, 27 H, Me_3Si), 1.37 (br. s, 6H, MeB). The mass spectrum had the base peak at *m/e* 169 $[(Me_3Si)_2CB]^+$ and prominent peaks at 257 (64; $[M - Me]^+$), 184 (11; $[M - Me_4Si]^+$) and 73 (58).

(b) A mixture of IV (0.08 g) and MeOH (4 cm^3) was stirred overnight at room temperature, then evaporated under reduced pressure. The residue was extracted with pentane, and the pentane solution was filtered and evaporated to leave unchanged IV (0.068 g, 83%), as indicated by the ^1H and ^{11}B NMR spectra.

(c) A solution of IV (0.132 g, 0.39 mmol) in Et_2O (3 cm^3) was added dropwise to $LiAlH_4$ (0.16 g, 3.5 mmol) in Et_2O (4 cm^3) under Ar. The mixture was stirred for 6 h at room temperature, then set aside overnight. The solvent was removed and the residue extracted with pentane. The pentane solution was filtered and the solvent evaporated to leave unchanged IV (0.12 g, 90%), as indicated by ^1H and ^{11}B NMR spectroscopy.

Reaction of $TsiB(OMe)_2$ *with MeLi*

A solution of MeLi in ether (1.0 cm^3 of 0.85 *M* solution) was added dropwise at room temperature under Ar to a solution of $TsiB(OMe)_2$ (0.12 g, 0.40 mmol) in Et_2O (2 cm^3) under nitrogen. The mixture was stirred for 18 h, then the solvent was removed and the residue extracted with pentane. The pentane solution was filtered and evaporated, and the residue sublimed to give $TsiBMe_2$ (in good but unrecorded yield), with properties identical to that obtained from IV (see above).

Reaction of TsiLi with $AlCl_3$

A mixture of TsiH (2 g, 8.7 mmol) in THF (30 cm^3) with MeLi in Et_2O (8 cm^3 of 1.2 *M* solution; made from MeCl under argon) was stirred for 20 h at room temperature followed by 0.5 h under reflux (cf. ref. 11). The cooled solution was treated with Me_3SiOEt (2 mmol), then added dropwise with stirring to a solution of $AlCl_3$ (1.3 g, 10 mmol) in ether (30 cm^3) under argon at room temperature, and the mixture was subsequently refluxed for 3 h. The solvent was then removed, and the residue was extracted with heptane. The heptane solution was concentrated and cooled, to give crystals of $TsiAlCl_2$ (0.43 g, 15%), m.p. > 300°C (Found: C, 36.7; H, 7.7; Cl, 21.1. $C_{10}H_{27}AlCl_2Si_3$ calcd.: C, 36.45; H, 8.3; Cl, 21.5%); IR (Nujol) 450 and 480 cm^{-1} ν(Al–Cl); ^1H NMR (C_6D_6) δ 0.45 (s, Me_3Si); mass spectrum, *m/e* 313 (50, $[M-Me]^+$), 293 (5, $[M-Cl]^+$), 237 (93; contains one Cl), 201 (68), 129 (21), 93 (32), 73 (100). There were no peaks from fragmentation of dimers such as are usually found [13] in mass spectra of alkylaluminium dihalides. The molecular weight (as determined in cyclohexane by the freezing point depression method with a Grant Type LE8 50Hz instrument) was 321 (Calcd.: 329).

The residue from the heptane extraction was treated with MeOH, and the solvent removed. The residue was extracted with pentane and the pentane solution was filtered, then evaporated, and volatile materials were pumped off under vacuum, some TsiH (authentic ^1H NMR spectrum) being collected in a cold trap. The residue crystallized on standing, and was identified as $Tsi(CH_2)_4OH$ (0.53 g, 20%) by comparison of its spectra with that of an authentic sample (see below) (Found: C, 55.7; H, 11.4. $C_{14}H_{36}OSi_3$ calcd.: C, 55.2; H, 11.9%).

Reaction of TsiLi with $TsiO(CH_2)_4I$

A solution of $TsiO(CH_2)_4I$ (2.75 g, 10.1 mmol) (made from Me_3SiI and THF [13]) in Et_2O (20 cm^3) was added dropwise under argon with stirring to a solution of TsiLi made from TsiH (2 g, 8.7 mmol) in THF (23 cm^3) and MeLi (10 mmol) in ether (7 cm^3) (with destruction of the residual MeLi by addition of Me_3SiOEt (3 mmol)). The mixture was stirred at room temperature overnight, then the solvent was removed and the residue was treated with water. Extraction with pentane, followed by washing, drying ($MgSO_4$), and evaporation of the pentane solution and fractional distillation of the liquid residue gave $Tsi(CH_2)_4OSiMe_3$ (2.5 g, 78%), b.p.

110–120°C/4 mmHg; ^{1}H NMR (CCl_4), 0.33 (s, 9H, Me_3SiO), 0.38 (s, 27H, Tsi), 1.60 (unres. m, 6H, CH_2), 3.53–3.84 (m, 2H, OCH_2); ^{13}C NMR, δ 62.0 (C^1), 34.3 (C^2), 31.8 (C^3), 26.6 (C^4), 4.15 (C^5), 2.9 (C^6), −0.4 (C^7) (numbering $(Me^6_3Si)_3C^5C^4H_2C^3H_2C^2H_2C^1H_2OSiMe^7_3$). The mass spectrum showed peaks (among others) at *m/e* 376 ($[M]^+$), and 361 ($[M-Me]^+$).

Preparation of Tsi(CH$_2$)$_4$OH

A solution of $Tsi(CH_2)_4OSiMe_3$ (1.3 g, 3.5 mmol) in MeOH (5 cm^3) containing a few drops of 0.1 *M* aqueous HCl was stirred at room temperature for 15 min. The solvent was evaporated under vacuum to leave a thick liquid, which crystallized on standing to give $Tsi(CH_2)_4OH$ (0.77 g, 73%), m.p. 70–75°C (Found: C, 55.1; H, 11.6. $C_{14}H_{36}OSi_3$ calcd.: C, 55.2; H, 11.9%); ^{1}H NMR (CCl_4), δ 0.13 (s, 27H, Me_3Si), 1.4–1.7, (unres. m, 6H, CH_2), 2.38 (s, 1H, OH; disappeared on shaking with D_2O), 3.60 (br t, 2H, OCH_2); ^{13}C NMR, δ 62.5 (C^1), 34.4 (C^2), 31.2 (C^3), 26.6 (C^4), 4.20 (C^5), 3.0 (C^6) (for numbering see preceding experiment). The mass spectrum showed peaks (among others) at *m/e* 303 ($[M-H]^+$) and ($[M-Me]^+$).

Reaction of Tsi(CH$_2$)$_4$OH with NaOMe/MeOH

A solution of $Tsi(CH_2)_4OH$ (0.05 g) in 4 *M* NaOMe/MeOH (2 cm^3) was stirred at room temperature for 2 h. The solvent was removed under vacuum and the residue was extracted with pentane. The pentane solution was filtered and evaporated, to leave semi-solid (0.047 g, 93%), identified as $(Me_3Si)_2CH(CH_2)_4OSiMe_3$; ^{1}H NMR ($CCl_4$), δ −0.40 (m, CH), 0.21 (s, 9H, Me_3SiO), 0.23 (s, 18H, Me_3Si), 1.7 (unres. m, 6H, CH_2), 3.60 (br t, 2H, OCH_2); ^{13}C NMR δ 62.6 (C^1), 34.4 (C^2), 31.1 (C^3), 26.3 (C^4), 4.1 (C^5), 2.8 (C^6), 1.0 (C^7) (for numbering see above).

Preparation of TsiGa(OH)Me

A solution of TsiLi was made from TsiH (2 g, 8.7 mmol) in THF (30 cm^3) by treatment with MeLi (10 mmol) in Et_2O (8 cm^3) under argon as described above. To this solution under reflux (without removal of the excess of MeLi) a solution of $GaCl_3$ (0.53 g, 3 mmol) in Et_2O (30 cm^3) was added dropwise under argon and the mixture was subsequently refluxed for 3 h. The solvent was then removed and the residue extracted with pentane. The pentane solution was evaporated to leave a thick liquid, which was sublimed at 100°C/0.1 mmHg to give a solid, m.p. 186–187°C, thought to be TsiGa(OH)Me (Found: C, 39.4; H, 9.3. $C_{11}H_{31}GaOSi_3$ calcd.: C, 39.6; H, 9.3%); IR (Nujol) ν(O–H), 3620 cm^{-1}; ^{1}H NMR (C_6D_6), 0.65 (s, 3H, CH_3), 0.72 (s, 27H, Me_3Si), 2.45 (s, 1H, OH). The mass spectrum showed peaks (among others) at *m/e* 317 $[M-Me]^+$), and 301 ($[M-MeH-Me]^+$).

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