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TRIMETHYLSILYLMETHYL AND BIS(TRIMETHYLSILYL)METHYL DERIVATIVES OF BORON, ALUMINIUM, CADMIUM AND MERCURY *

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Summary

Reactions between bis(trimethylsilyl)methyl lithium and the chlorides ECl_3 ($E = B$ or Al) yield the di[bis(trimethylsilyl)methyl] derivatives $[(Me_3Si)_2CH]_2-ECl$. The boron compound may be converted by compounds HX ($X = OH, NH_2, NMe_2$) in the presence of bases to compounds $[(Me_3Si)_2CH]_2BX$ but the aluminium-carbon bond in $[(Me_3Si)_2CH]_2AlCl$ is easily broken with formation of $(Me_3Si)_2CH_2$. Bis(trimethylsilylmethyl)aluminium chloride has been made from tris(trimethylsilylmethyl)aluminium and aluminium chloride. Bis(trimethylsilyl)methyl lithium reacts with the chlorides ECl_2 ($E = Cd$ or Hg) to give the derivatives $[(Me_3Si)_2CH]_2E$. The cadmium compound is hydrolysed by water or methanol, but not the mercury compound, which reacts with mercury(II) halides to give compounds $(Me_3Si)_2CHHgX$ ($X = Cl, Br$ or I). Di[1,1'-bis(trimethylsilyl)ethyl]mercury has also been made.

Introduction

Many trimethylsilylmethyl and bis(trimethylsilyl)methyl derivatives of metals and non-metals may be obtained, even when corresponding methyl or ethyl derivatives cannot be isolated [1,2]. However, few compounds of boron and aluminium with these large alkyl groups have been described. Tris(trimethylsilyl)borane [3] is made from boron trifluoride/ether and the organolithium compound, and tris(trimethylsilyl)alane is obtained as an etherate from the reaction between aluminium chloride and the Grignard reagent [4]. The uncomplexed aluminium compound $(Me_3SiCH_2)_3Al$ may be made from the mercurial and metallic aluminium [5] and the compound $[Me_3Si(CH_2)_3]_3Al$ from 3-trimethylsilylprop-1-ene and diisobutylaluminium hydride [6].

The chemistry of these trimethylsilylmethyl compounds has not been very

* No reprints available.

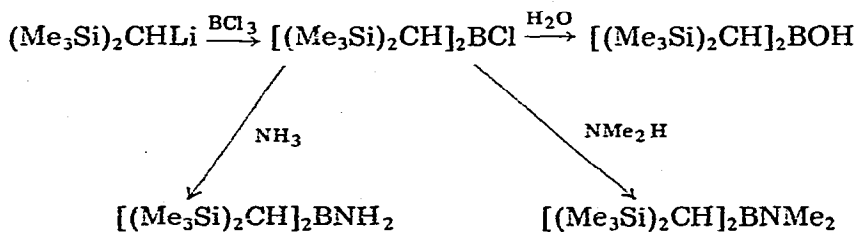
thoroughly explored, but it appears to be very similar to that of the compounds with smaller alkyl groups. Thus, the compound $(\text{Me}_3\text{SiCH}_2)_3\text{B}$ is unreactive towards water, but easily decomposed by alkaline hydrogen peroxide with cleavage of the B—C bond and formation of the alcohol $\text{Me}_3\text{SiCH}_2\text{OH}$. The compound $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ is, like other alkylaluminium compounds, spontaneously inflammable in air and very easily hydrolysed by water.

Results and discussion

In attempts to make derivatives of boron and aluminium with the larger bis(trimethylsilyl)methyl group, the trichlorides were treated with an excess of the lithium reagent [7]. Even under forcing conditions, the compounds isolated were $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{ECl}$ (E = B or Al) suggesting that replacement of the third chloride by $(\text{Me}_3\text{Si})_2\text{CH}$ is prevented by the large groups already attached to the Group III element. Similar difficulties have been noted in the preparation of tri(cyclohexyl)aluminium [8], and in the reaction between mesitylmagnesium bromide and boron trifluoride. In boiling ether, the product is $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{BF}$; formation of $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_3\text{B}$ requires prolonged heating under reflux in toluene [9]. In contrast, tri[bis(trimethylsilyl)methyl] derivatives of scandium and yttrium may be obtained in boiling ether [10].

Di[bis(trimethylsilyl)methyl]boron chloride was isolated as a volatile white crystalline solid, only slowly hydrolysed by moist air. It could be converted quantitatively by water in dioxan to the borinic acid $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BOH}$. This is a remarkably unreactive compound, apparently unchanged in moist air, and subliming in vacuum without decomposition. Dialkylborinic acids R_2BOH (R = n-Pr or n-Bu), however, are easily oxidised to the boronic acids $\text{RB}(\text{OH})_2$ or dehydrated to the anhydrides $(\text{R}_2\text{B})_2\text{O}$ [11–13]. In its inertness, the compound $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BOH}$ resembles the dimesityl derivative $(\text{Me}_3\text{C}_6\text{H}_2)_2\text{BOH}$ [9]. Di[bis(trimethylsilyl)methyl]borinic acid is almost insoluble in water. It is a very weak acid; solutions in ethanol do not react with pyridine and the solid obtained on evaporation of a mixture of the borinic acid and an equivalent amount of sodium hydroxide in ethanol appears to be simply a mixture of starting materials. There is no evidence for formation of a salt $\text{Na}^+[\text{BR}_2(\text{OH})_2]^-$ like that described when R = Me [14].

The chloride $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ reacted with ammonia in the presence of triethylamine to give the amido compound $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BNH}_2$ which was monomeric in freezing benzene. More forcing conditions (16 h at 90°C) were required for the reaction between $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ and dimethylamine.



The di[bis(trimethylsilyl)methyl]boron derivatives were not attacked by alkaline

hydrogen peroxide under conditions which normally give complete removal of large alkyl groups from boron [15].

Bis(trimethylsilylmethyl)aluminium chloride (easily made from tris(trimethylsilyl)methylaluminium and aluminium(III) chloride) and di[bis(trimethylsilyl)methyl]aluminium chloride were dimeric in freezing benzene. They were very readily hydrolysed or oxidised in moist air. Diethyl ether was easily pumped away from the di[bis(trimethylsilyl)methyl] derivative, even though it is held tenaciously by diethylaluminium chloride under similar conditions.

Routes to the bis(trimethylsilyl)methyl derivatives of boron and aluminium were also sought via the mercury compound $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ [16]. This failed to react with aluminium foil under conditions similar to those used to make $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$, but gave bis(trimethylsilyl)methylmercury chloride by reaction with boron trichloride. The boron-containing product has not been identified although the corresponding reaction between diphenylmercury and boron trichloride has been used for the preparation of arylboronic acids [17].

The compounds $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$, $[(\text{Me}_3\text{Si})_2\text{CMe}]_2\text{Hg}$ and $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Cd}$ were made from mercury(II) or cadmium(II) chlorides and the corresponding trimethylsilylalkyllithium. The cadmium compound was hydrolysed by water or methanol. The dialkyl $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ reacted with mercury(II) halides to give the compounds $[(\text{Me}_3\text{Si})_2\text{CH}]\text{HgX}$ ($X = \text{Br}$, or I), as crystalline solids. The bromide decomposed during several months at 20°C with formation of the dialkyl $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ and HgBr_2 ; disproportionation of the iodide, like that of the analogous $\text{Me}_3\text{SiCH}_2\text{HgI}$ [18] was more rapid and the compound could not be obtained analytically pure.

Vibrational spectra

In the compounds $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BX}$ ($X = \text{OH}$, or NH_2) the IR peaks corresponding to O—H or N—H stretching are sharp, showing that intermolecular hydrogen bonding is prevented by the large alkyl groups. The IR spectrum of solid $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BOH}$, with a sharp peak at 3650 cm^{-1} , thus resembles that of Me_2BOH vapour [14]. The boron derivatives $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BX}$ ($X = \text{Cl}$, OH , NH_2 , NMe_2) also show, besides the bands characteristic of $(\text{Me}_3\text{Si})_2\text{CH}$ group (Table 1 and ref. 7) two additional medium or strong bands between 1200 and 1250 cm^{-1} .

These bands, which are absent in the spectrum of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCl}$ must be associated with the C_2BX skeleton [14,19]. Other peaks associated with this part of the molecule cannot be clearly distinguished from absorptions of the bis(trimethylsilyl)methyl group.

The IR spectrum of solid $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCl}$ is like that of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$. Several sets of peaks associated with the $(\text{Me}_3\text{Si})_2\text{CH}$ group are weaker in the aluminium than in the boron compound and this may reflect the more symmetrical dimeric structure of the aluminium derivative. The vibrational spectra of bis(trimethylsilylmethyl)aluminium chloride showed peaks characteristic of the Me_3SiCH_2 group [5,20]. It was possible to obtain good Raman spectra, which showed the strong shifts of 161p , 627p , 692dp cm^{-1} found in $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ [5] and $(\text{Me}_3\text{SiCH}_2)_2\text{E}$ ($\text{E} = \text{Sn}$, Pd) [20]. There were additional strong polarised lines at 285 (ν_3) [21], 351 (ν_2), 536 and 584 cm^{-1} as in other dialkylaluminium chloride dimers [22]. In spectra of dimethyl- and diethyl-aluminium

TABLE 1

VIBRATIONAL SPECTRA (cm^{-1})

All $(\text{Me}_3\text{Si})_2\text{CH}$ derivatives	IR	2960—2090 ($\nu(\text{CH})$), 1605—1390, 1295—1250 ($\delta(\text{CH}_3)$), 1070—1005 ($\nu(\text{Si}_2\text{C})$), 996—845, 786—721 ($\rho(\text{CH}_3)$), 690—610 ($\nu(\text{SiC}_3)$), 340—280 ($\delta(\text{SiC}_3)$)
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$	IR (mull)	1225m, 1205s, 1030m, 1015(sh), 985s, 795m, 766w, 566w, 521w, 491w
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BOH}$	IR (mull)	3650m ($\nu(\text{OH})$), 1222s, 1082w, 1037m, 1017m, 1002w, 939w, 781w, 765w, 737w, 726w, 545w, 525w
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BNH}_2$	IR (mull)	3510w, 3430w ($\nu(\text{NH})$), 1609m ($\delta(\text{NH}_2)$), 1225m, 1205s, 1090w, 1040m, 1000m, 895s, 775w, 735w, 505s
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BNMe}_2$	IR (mull)	3040w, 2820w, 2800w, 1510(sh), 1500m, 1210s, 1130m, 1100m, 1035m, 1005m, 975s, 955w, 760m, 730w, 570w, 505w
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCl}$	IR (mull)	1080m, 1015m, 1006(sh), 570w, 510w
$(\text{Me}_3\text{SiCH}_2)_2\text{AlCl}$	Raman	692sdp, 655w, 627vsp, 584mp, 536sp, 489vw, 351mp, 286mp, 242sdp, 216mdp, 161mp, 116mdp, 106wp
	IR (film)	580s
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$	Raman	580s, 497vsp, 425w, 340mp, 254m, 205m, 118mp, 82w
	IR (film)	615s, 510m, 340w, 280m
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Cd}$	Raman	597m, 482vsp, 337sp, 243m, 196(sh), 170s
	IR (film)	610s, 490m, 340m, 280m, 240w

chlorides, there is only one Raman peak (ν_1) between 500 and 600 cm^{-1} , but the spectrum of dibutylaluminium chloride is more complex. Strong interaction between Al—C and Si—C vibrations seems likely in the trimethylsilylmethyl compound.

As expected, spectra of di[bis(trimethylsilyl)methyl]-cadmium and -mercury are almost identical*. The MC_2 ($\text{M} = \text{Cd}$ or Hg) stretching frequencies in dimethylcadmium (466, 538 cm^{-1}) are less than in dimethylmercury (515, 550 cm^{-1}) [23]. In $(\text{Me}_3\text{Si})_2\text{CH}$ -derivatives, vibrations associated with the C—M—C skeleton are expected to interact with the symmetrical vibrations of the Si_2C group (usually at 480—510 cm^{-1}) [7], but it is interesting that in both IR and

* Since the completion of our work, we have seen the paper by Glockling et al. [29], which gives vibrational and mass spectra of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ and $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{HgCl}$. Our results and theirs are similar.

Raman spectra frequencies are 15–20 cm^{-1} lower in the cadmium compound than in the mercury analogue.

Mass spectra

In mass spectra (Table 2), empirical formulae of ions containing silicon, boron, mercury, cadmium and halogen may almost always be assigned from isotope patterns. Where this has not been possible accurate mass measurements have been made. Some proposed fragmentations are also supported by metastable peaks.

For the compounds $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BX}$ ($\text{X} = \text{Cl}, \text{OH}, \text{NH}_2$ or NMe_2), several fragmentation paths are observed. In all cases, prominent peaks arise from loss

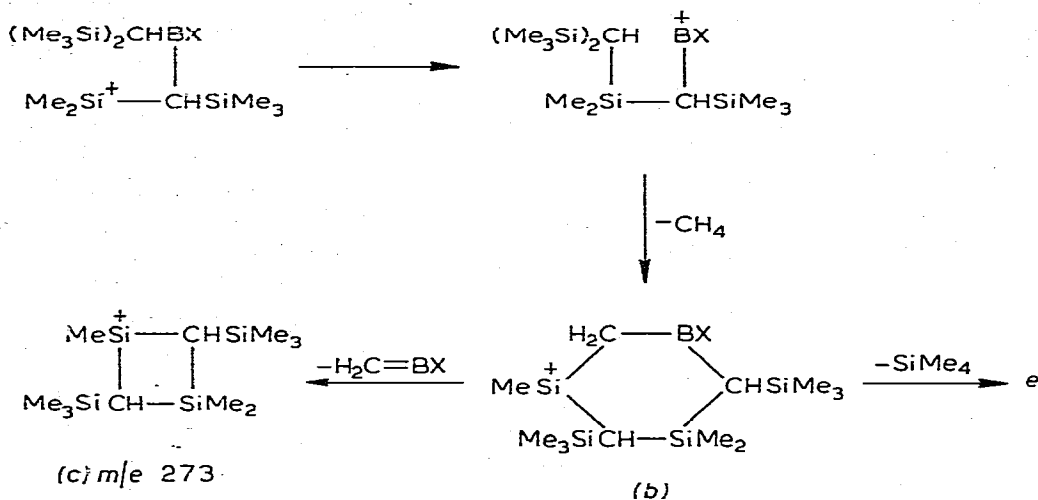
TABLE 2

MASS SPECTRA ^a

$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$: 349(26) <i>P</i> – Me; 333(0.3) ^b ; 273(3) ^c ; 265(5) <i>P</i> – Me – Me_4Si ; 241(9) ^d ; 201(0.5) ^f ; 185(3) ^g ; 97(3); 73(31) ^k
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BOH}$: 331(2) <i>P</i> – Me; 315(25) ^b ; 273(11) ^c ; 259(1) <i>P</i> – Me – $\text{Me}_2\text{Si}=\text{CH}_2$; 257(1) <i>P</i> – Me – Me_3SiH ; 241(6), ^d ; 227(7) ^e ; 201(1) ^f ; 185(2) ^g ; 145(2) ^h ; 129(10) ⁱ ; 73(25) ^k . Metastable peaks: 299.8 (331→315). 236.6 (315→273); 163.6 (315→227)
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BNH}_2$: 330.2105(36), <i>P</i> – Me (¹² C ₁₃ ¹ H ₃₇ ¹¹ B ¹⁴ N ²⁸ Si ₄ calcd.: 330.2096); 314(5) ^b ; 273(5) ^c ; 241(10) ^d ; 226(5) ^e ; 201(1) ^f ; 186(9) $[(\text{Me}_3\text{Si})_2\text{CHBNH}_2]^+$; 129(13) ⁱ ; 73(19) ^k . Metastable peak: 298.8 (330→314)
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BNMe}_2$: 373 (1.3) <i>P</i> , 358 (4.2) <i>P</i> – Me; 330(0.7); 329(2.2) <i>P</i> – NMe_2 ; 315(0.4) <i>P</i> – Me – $\text{MeN}=\text{CH}_2$; 313(0.6) <i>P</i> – Me – Me_2NH ; 273(0.9) ^c ; 270(0.6) <i>P</i> – Me – Me_4Si ; 257(0.2); 241(0.9) ^d ; 214(30.0) <i>P</i> – $(\text{Me}_3\text{Si})_2\text{CH}$; 198(0.8); 185(0.9); 169(0.9); 157(1.8); 129(13.0) ⁱ ; 102(7.2); 97(1.8); 72(29) ^k . Metastable peaks: 162.5 (358→241); 122.7 (373→214); 77.8 (214→129).
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCl}$: 365 <i>P</i> – Me; 273 ^c ; 145 ^h and 65, possibly from hydrolysis. See text.
$(\text{Me}_3\text{SiCH}_2)_2\text{AlCl}$: 221(23), <i>P</i> – Me; 205(3), ^b ; 169(1) $[\text{Me}_2\text{SiCH}_2\text{AlCl}_2]^+$; 149(2) $[\text{Me}_3\text{SiCH}_2\text{AlCl}]^+$; 129(11) ⁱ . 113(2) $[\text{MeSiCl}_2]^+$; 93(9) $[\text{Me}_2\text{SiCl}]^+$; 73(23) ^k .
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$: 520(5) <i>P</i> ; 505(22) <i>P</i> – Me; 361(1), $[(\text{Me}_3\text{Si})_2\text{CHHg}]^+$; 245(2) $[\text{Me}_3\text{SiCHSiMe}_2]_2\text{Hg}^{++}$; 202(4) Hg^+ ; 159(2) $[(\text{Me}_2\text{Si})_2\text{CH}]^+$; 145(4), ^h ; 129(25) ⁱ ; 115(1); 113(1); 85(4); 83(1); 73(13) ^k ; 59(4). Metastable peak 491 (520→505).
$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Cd}$: 432(3) <i>P</i> ; 417(23) <i>P</i> – Me; 271(3) <i>P</i> – $(\text{Me}_3\text{Si})_2\text{CH}$; 201(11) $[(\text{Me}_3\text{SiCHSiMe}_2)_2\text{Cd}]^{++}$; 159(3) $[(\text{Me}_2\text{Si})_2\text{CH}]^+$; 145(10) ^g ; 129(25) ^h ; 85(7); 73(15)
$(\text{Me}_3\text{Si})_2\text{CHHgCl}$: 381(7) <i>P</i> ; 202(3) Hg^+ ; 179(2) $(\text{Me}_3\text{Si})_2\text{CHCl}$ – Me; 145(3) ^h ; 129(6) ⁱ ; 113(1); 100(1); 93(5) $[\text{Me}_2\text{SiCl}]^+$; 85(38) ^j ; 73(17) ^k .
$(\text{Me}_3\text{Si})_2\text{CHHgBr}$: 425(33) <i>P</i> – Me; 223(4) $(\text{Me}_3\text{Si})_2\text{CHBr}$ – Me; 202(3) Hg^+ ; 145(3) ^h ; 137(2) $[\text{Me}_2\text{SiBr}]^+$; 129(6) ⁱ ; 85(20) ^j ; 73(12) ^k .
$(\text{Me}_3\text{Si})_2\text{CHHgI}$: 473(8) <i>P</i> – Me; 271(10) $(\text{Me}_3\text{Si})_2\text{CHI}$ – Me; 243(1); 202(6) Hg^+ ; 185(3) $[\text{Me}_2\text{SiI}]^+$; 145(6) ^h ; 129(13) ⁱ ; 85(21) ^j ; 73(19) ^k .

^a Recorded with an AEI MS30 instrument at 70 eV. *m/e* values (intensities as % of total current, in parentheses) and possible assignments. Parent ion *P*. Only peaks for ²⁸Si, ¹¹B, ³⁵Cl, ⁷⁹Br, ¹¹⁴Cd and ²⁰²Hg given. ^b *P* – Me – CH_4 . ^c 273 $[\text{Me}_3\text{SiCHSiMe}_2\text{CHSiMe}_3\text{SiMe}]^+$. There are several possible isomers of this and related ions. ^d 241 *P* – Me – Me_3SiX ($\text{X} = \text{Cl}, \text{OH}, \text{NH}_2$ or NMe_2). ^e *P* – Me – CH_4 – SiMe_4 . ^f 201 $[\text{Me}_3\text{SiCHSiMe}_2\text{CH}_2\text{SiMe}]^+$. ^g 185 201 – CH_4 . ^h 145 $[\text{Me}_2\text{SiCH}_2\text{SiMe}_3]^+$. ⁱ 129 $[\text{Me}_2\text{SiCH}=\text{SiMe}_2]^+$. ^j 85 $[\text{H}_2\text{CCH}_2\text{CH}_2\text{SiMe}]^+$. ^k 73 $[\text{Me}_3\text{Si}]^+$.

of a methyl group from the parent ion, and further peaks indicate elimination of CH_4 , Me_4Si , Me_3SiH , or $\text{Me}_2\text{Si}=\text{CH}_2$, or, for $[(\text{Me}_2\text{Si})_2\text{CH}]_2\text{BNMe}_2$, of Me_2NH and perhaps $\text{MeN}=\text{CH}_2$. For the two amido compounds, there are strong peaks corresponding to $[(\text{Me}_3\text{Si})_2\text{CHBNR}_2]^+$ ($\text{R} = \text{H}$ or Me); the peak for the dimethyl-amido compound is the strongest in the spectrum. A metastable peak shows further elimination of Me_2BNMe_2 . For $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BOH}$ elimination of methane is particularly easy and the peak at m/e 315 is very strong. Metastable peaks then indicate further transformations giving peaks at m/e 273 and 227. The isotope pattern of the first of these shows that it arises from a species which does not contain boron. This may be a cyclic cation formed by transfer of alkyl groups between silicon and boron.

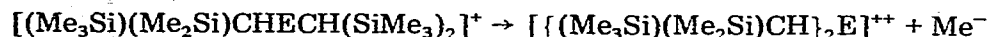


Details of these rearrangements cannot at present be delineated, but similar cyclic cations have been proposed in fragmentations of other polysilanes [24]. The ion at m/e 273 is also prominent in the spectrum of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCl}$. Analogous rearrangements of ions derived from $[\text{Me}_3\text{SiCH}_2]_2\text{AlCl}$ lead to the ion at m/e 129, which could have a cyclic structure or be $[\text{Me}_2\text{SiCH}=\text{SiMe}_2]^+$, a silicon analogue of the 1,1',3,3'-tetramethylallyl ion.

The aluminium derivatives R_2AlCl [$\text{R} = \text{Me}_3\text{SiCH}_2$ or $(\text{Me}_3\text{Si})_2\text{CH}$] showed no ions from fragmentation of dimers in spectra run at 20 eV. In contrast, ions containing two aluminium atoms have been observed when $\text{R} = \text{Me}$ or Et [24]. For $(\text{Me}_3\text{SiCH}_2)_2\text{AlCl}$ the fragmentation pattern (Table 2) was easily understood, but there was also a peak at m/e 169 from loss of methyl from $\text{Me}_3\text{SiCH}_2\text{AlCl}_2$. For $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCl}$, the peaks at m/e 145 ($[\text{Me}_3\text{SiCH}_2\text{SiMe}_2]^+$) and 65 ($[\text{Me}_2\text{SiCH}_2\text{SiMe}_2]^{++}$) probably indicate some hydrolysis in the mass spectrometer and so this spectrum has not been analysed further.

For the compounds R_2E ($\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$, $\text{E} = \text{Cd}$ or Hg), the most prominent peaks are those corresponding to loss of methyl from the parent ions, and the peak at m/e 129. About the same proportion of the total current is carried by E-containing fragments in the cadmium as in the mercury compound, but the peak from Hg^+ is stronger than that from Cd^+ and the peak from RCd^+ is stronger than that from RHg^+ . The ions R^+ are weak; in contrast, they give the

strongest peaks in the mass spectra of dimethyl-, dibenzyl- and dibutyl-mercury [26]. As in the mass spectrum of $(\text{Me}_3\text{SiCH}_2)_2\text{Hg}$ [18], peaks for doubly charged ions are observed. These show the reactions:



(E = Cd or Hg)

Most of the ion current from the compounds $(\text{Me}_3\text{Si})_2\text{CHHgX}$ (X = Cl, Br or I) is carried by fragments derived from the trimethylsilyl-substituted alkyl group. The only significant species containing mercury are the parent ions minus methyl, and Hg^+ . There are also peaks assigned to $[(\text{Me}_3\text{Si})(\text{Me}_2\text{Si})\text{CHX}]^+$ presumably formed by elimination of mercury atoms from the ions $[(\text{Me}_3\text{Si})(\text{Me}_2\text{Si})\text{CHHgX}]^+$. Similar eliminations have been observed in mass spectra of arylmercury halides [26].

Experimental

Air and moisture were excluded as far as possible from all reactions. NMR spectra were recorded on a Perkin-Elmer EM360 instrument using samples in benzene or toluene. Chemical shifts were measured from the solvent peak, assumed to be at τ 2.73 for benzene and τ 7.66 for toluene.

Di[bis(trimethylsilyl)methyl]boron chloride

Boron trichloride (4.74 g, 40.4 mmol) at -63°C was added to $(\text{Me}_3\text{Si})_2\text{CHLi}$ (57.5 mmol) in ether (125 ml). The mixture was warmed slowly from -63°C , heated under reflux for $2\frac{1}{2}$ h, and filtered. After removal of solvent, the residue was sublimed to give boron trichloride/diethyl ether (1.0 g, 5.2 mmol. Subl. $40^\circ\text{C}/2$ Torr, m.p. 54°C (lit. [27], m.p. 55°C), identified by its NMR spectrum) and di[bis(trimethylsilyl)methyl]boron chloride, m.p. 48°C . Yield 3.5 g, 38% based on $(\text{Me}_3\text{Si})_2\text{CHLi}$. (Found: C, 46.2; H, 10.3. $\text{C}_{14}\text{H}_{38}\text{BClSi}_4$ calcd.: C, 46.2; H, 10.4%.) NMR: τ 8.50 (CH); 9.73 (Me_3Si). In a second experiment, solvent ether was pumped from the lithium reagent (35 mmol) and replaced by toluene (50 ml). After the addition of boron trichloride (1.30 g 11.6 mmol) in ether (2 ml), the mixture was heated under reflux for 12 h, but $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ was the only compound isolated after filtration and removal of solvent. Di[bis(trimethylsilyl)methyl]boron chloride was recovered unchanged after 16 h at 240°C in a sealed tube. It could be handled rapidly in dry air, but in moist air it was hydrolysed slowly to the borinic acid $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BOH}$.

Reactions of di[bis(trimethylsilyl)methyl]boron chloride

(a) *With water.* The chloride $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ (0.589 g, 1.59 mmol) in dioxan (2 ml) was treated with water (2 ml) and the mixture was left at 20°C for 16 h. After removal of solvent, di[bis(trimethylsilyl)methyl]borinic acid was sublimed at $55-60^\circ\text{C}/10^{-3}$ Torr. M.p. 35°C . Yield 0.35 g (64%). (Found: C, 48.7; H, 11.3. $\text{C}_{14}\text{H}_{39}\text{BOSi}_4$ calcd.: C, 48.6; H, 11.3%.) NMR: τ 5.48 (OH?); 8.41 (CH); 9.60 (Me_3Si).

(b) *With ammonia.* Ammonia (2.89 mmol) was condensed into a mixture of the chloride $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ (1.43 mmol) and triethylamine (1.67 mmol) in

ether (25 ml) at -78°C . The excess of ammonia (1.52 mmol) was recovered as the solution warmed, and a white precipitate was filtered off. Ether was removed from the filtrate under reduced pressure and aminodi[bis(trimethylsilyl)methyl]borane sublimed at $70^{\circ}\text{C}/10^{-3}$ Torr, m.p. 66°C . Yield 0.2 g (40%). (Found: C, 48.6; H, 11.4, N, 3.4. $\text{C}_{14}\text{H}_{40}\text{BNSi}_4$ calcd.: C, 48.6, H, 11.6; N, 4.0%.) NMR: τ 9.67 (Me_3Si). Another resonance which, at 90 MHz, is incompletely resolved from the main peak may correspond to the CH group.

(c) *With dimethylamine.* $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ (1.0 g, 2.75 mmol) and dimethylamine (1.0 g, 22 mmol) were heated in a sealed tube at 90°C for 16 h. The excess of dimethylamine was removed, and the residue extracted with ether. The dimethylammonium chloride was filtered off and, after removal of solvent, di[bis(trimethylsilyl)methyl](dimethylamino)borane was distilled, b.p. $90^{\circ}\text{C}/10^{-3}$ Torr. Yield 0.7 g (70%). (Found: C, 51.6; H, 11.4; N, 3.5. $\text{C}_{16}\text{H}_{44}\text{BNSi}_4$ calcd.: C, 51.5; H, 11.8; N, 3.7%.) NMR: τ 7.33 (NMe_2); 9.73 (Me_3Si). The CH resonance is probably under the main peak. IR and NMR spectra showed that a sample of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BNMe}_2$ left 16 h in the open air was unchanged.

(d) *With methyllithium.* An excess of methyllithium (5 mmol) in ether was added to $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ (0.60 g, 1.65 mmol) in ether (10 ml). After the mixture was heated under reflux for 5 h, $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ (0.48 g, 80%), identified by analysis, NMR and mass spectra, was recovered unchanged.

(e) *With hydrogen peroxide.* Hydrogen peroxide (10 ml, 30%) was added carefully at $40\text{--}45^{\circ}\text{C}$ to a mixture of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BCl}$ (1.00 g, 2.75 mmol) and sodium hydroxide (0.65 g) in tetrahydrofuran (25 ml) and ethanol (10 ml). The mixture was agitated at 55°C for 2 h. The aqueous layer was saturated with sodium carbonate, and extracted three times with ether. After removal of solvent from the combined extracts the residue was recrystallised from heptane and identified spectroscopically as starting material $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{BOH}$ (0.901 g, 2.6 mmol.). (Found: C, 48.0, H, 11.3. $\text{C}_{14}\text{H}_{39}\text{BOSi}_4$ calcd.: C, 48.6; H, 11.3%.)

Di[bis(trimethylsilyl)methyl]aluminium chloride

Aluminium chloride (2.92 g, 21.9 mmol) was added slowly to a stirred solution of $(\text{Me}_3\text{Si})_2\text{CHLi}$ (60.2 mmol) in ether (100 ml) at 0°C . The mixture was warmed to room temperature, then heated under reflux for $4\frac{1}{2}$ h, and the white precipitate of lithium chloride was filtered from the orange solution. Solvent was removed in vacuum and white crystals of the product $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCl}$ sublimed at $100^{\circ}\text{C}/10^{-3}$ Torr. Yield after sublimation 4.0 g, 47%. (Found: C, 44.3; H, 10.1; Al, 6.9; Cl, 9.1%; mol. wt., 790 (0.5 wt.% soln.). $\text{C}_{14}\text{H}_{38}\text{AlClSi}_4$ calcd.: C, 44.2; H, 10.0; Al, 7.1; Cl, 9.3%; mol. wt., 380.5.) NMR: τ 9.56 (Me_3Si); 10.19 (CH). In another experiment, bis(trimethylsilyl)methyllithium and aluminium chloride were heated under reflux in toluene for 14 h. The only product isolated was $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlCl}$.

Bis(trimethylsilylmethyl)aluminium chloride

Aluminium chloride (1.42 g, 10.7 mmol) was added to $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ [5] (6.01 g, 20.9 mmol) at 0°C . After 16 h at 20°C , the mixture was heated to 80°C for $2\frac{1}{2}$ h and then distilled. The colourless, inflammable liquid $(\text{Me}_3\text{SiCH}_2)_2\text{AlCl}$ was collected at $96\text{--}100^{\circ}\text{C}/10^{-3}$ Torr. Yield, 5.23 g, 70%. (Found: C, 40.3; H, 9.1; Al, 11.4, Cl, 14.7%; mol. wt., 394. $\text{C}_8\text{H}_{22}\text{AlClSi}_2$ calcd.: C, 40.7; H,

9.3; Al, 11.4; Cl, 14.8%; mol. wt., 236.5.) NMR: τ 9.64 (Me_3Si), 10.21 (CH_2), $^1J(^{13}\text{CH})$ 104 Hz.

In a similar experiment, a mixture of aluminium chloride (2.1 g, 16 mmol) and $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ (2.17 g, 8 mmol) at 80°C gave a thick pale brown liquid, from which some white crystals could be sublimed at $98^\circ\text{C}/10^{-3}$ Torr, but attempts to characterise the expected $\text{Me}_3\text{SiCH}_2\text{AlCl}_2$ were unsuccessful.

Di[bis(trimethylsilyl)methyl]mercury

Mercury(II) chloride (5.4 g, 20 mmol) in ether (100 ml) was added to a stirred solution of $[(\text{Me}_3\text{Si})_2\text{CHLi}]$ (51 mmol) in ether at 0°C . After 3 h, the mixture was hydrolysed with 1 *N* sulphuric acid, and the separated organic layer was dried with sodium sulphate. After removal of solvent, $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ was distilled, b.p. $80^\circ\text{C}/10^{-2}$ Torr, m.p. 32°C (lit. [16] b.p. $107^\circ\text{C}/4$ Torr; m.p. 35°C). Yield: 10.0 g, 97%. (Found: C, 32.8; H, 7.8; $\text{C}_{14}\text{H}_{38}\text{HgSi}_4$ calcd.: C, 32.4; H, 7.3%.) A similar preparation in tetrahydrofuran gave a lower yield (41%). NMR: τ 9.66 (Me_3Si); δ .86 (CH); $^2J(^{199}\text{HgCH})$ 141; $^1J(^{13}\text{CH})$ in Me_3Si 118 Hz.

Reactions of di[bis(trimethylsilyl)methyl]mercury

(a) *With aluminium.* $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ (2.0 g) and aluminium foil (1 g) were heated under reflux in toluene (50 ml) for 14 d and the resulting mixture filtered. The NMR spectrum of the filtrate showed only peaks due to solvent and the starting mercurial. Again, no organoaluminium compound was isolated when $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ was heated with aluminium wire and toluene in a sealed tube at 150°C for 1 week, but in this case the resulting solution appeared to contain several unidentified products.

(b) *With boron(III) chloride.* A mixture of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ (1.50 g, 2.88 mmol), boron(III) chloride (0.70 g, 6.00 mmol) and toluene (6 ml) was heated in a sealed tube at 100°C for 16 h. The tube was opened and boron(III) chloride (0.20 g, 1.70 mmol) and solvent were removed. The brown residue was sublimed to give white crystals of bis(trimethylsilyl)methylmercury chloride (1.06 g, 2.68 mmol), m.p. 89°C (lit. [101] m.p. $90\text{--}91^\circ\text{C}$). (Found: C, 21.4; H, 4.8. $\text{C}_7\text{H}_{19}\text{ClHgSi}_2$ calcd.: C, 21.3; H, 4.8%.) NMR: τ 9.63 (CH); 9.98 (Me_3Si). The properties of the solvent (^1H NMR: τ 9.59; IR: $\nu(\text{OH})$ 3500 cm^{-1} ; smell of HCl) suggested that the expected dichloro-derivative $(\text{Me}_3\text{Si})_2\text{CHBCl}_2$ was hydrolysed during manipulation.

(c) *With mercury(II) bromide.* A mixture of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ (1.06 g, 2.04 mmol), and mercury(II) bromide (0.74 g, 2.04 mmol) in ethanol (50 ml) was heated under reflux for 5 h. On cooling, a white solid precipitated. This was recrystallised from ethanol and shown to be bis(trimethylsilyl)methylmercury bromide, m.p. 29°C . Yield 0.66 g, 36% after recrystallisation. (Found: C, 18.8; H, 4.2. $\text{C}_7\text{H}_{19}\text{Si}_2\text{HgBr}$ calcd.: C, 19.0; H, 4.3%.) NMR: τ 9.53 (CH), 9.95 (Me_3Si).

(d) *With mercury(II) iodide.* $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$ reacted under similar conditions with mercury(II) iodide to give yellow crystalline bis(trimethylsilyl)-methylmercury iodide. This could not be obtained analytically pure since at 20°C it slowly deposited a black solid and a colourless liquid, but its formation was clearly shown by the strong peaks centered at m/e 473 in the mass spectrum. The compound $\text{Me}_3\text{SiCH}_2\text{HgI}$ [18] decomposes under similar conditions.

Di[bis(trimethylsilyl)methyl]cadmium

A suspension of anhydrous cadmium chloride (3.85 g, 21 mmol) in ether (100 ml) was added to a well-stirred solution of $(\text{Me}_3\text{Si})_2\text{CHLi}$ (42 mmol) in ether at 0°C , and the mixture was heated under reflux for $4\frac{1}{2}$ h. After removal of solvent the residue was extracted with three portions (50 ml) of benzene and then benzene was pumped away from the combined extracts. The residue was $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Cd}$, b.p. $75^\circ\text{C}/10^{-3}$ Torr. Yield 3 g, 34%. (Found: C, 39.0; H, 9.2. $\text{C}_{14}\text{H}_{38}\text{CdSi}_4$ calcd.: C, 39.0; H, 8.8%.) NMR: τ 9.70 (Me_3Si), 10.33 (CH).

The compound $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Cd}$ (0.387 g, 0.895 mmol) was treated with methanol (1.79 mol). The volatile material was pumped away and identified spectroscopically as $(\text{Me}_3\text{Si})_2\text{CH}_2$, and the white residue was dimethoxycadmium (0.140 g, 85%). (Found: C, 11.5; H, 3.0. $\text{C}_2\text{H}_6\text{CdO}_2$ calcd.: C, 11.6, H, 2.9%.) This is insoluble in hydrocarbons and appears, like the zinc and magnesium compounds [28], to be polymeric.

1-Chloro-1,1'-bis(trimethylsilyl)ethane

Methylolithium (60 mmol) in ether was added slowly to a well-stirred solution of dichlorobis(trimethylsilyl)methane (12.2 g, 53 mmol) in ether (150 ml), and the mixture was heated under reflux for 6 h. The white precipitate was filtered off, the solvent was pumped away, and $(\text{Me}_3\text{Si})_2\text{CMeCl}$ was distilled, b.p. $76^\circ\text{C}/6$ Torr. Yield: 7.13 g, 64%. (Found: C, 46.1; H, 10.5. mol. wt. (mass spectrum), 208. $\text{C}_8\text{H}_{21}\text{ClSi}_2$ calcd.: C, 46.1; H, 10.1%. mol. wt. 208.) NMR: τ 8.36 (Me), 9.73 Me_3Si).

Di[1,1'-bis(trimethylsilyl)ethyl]mercury

$(\text{Me}_3\text{Si})_2\text{CMeCl}$ (2.3 g, 11 mmol), lithium powder (1.5 g) and diethyl ether (100 ml) were heated under reflux for 49 h. The excess of lithium was filtered off to leave a clear solution from which an aliquot was titrated with 0.1 N HCl. The concentration was 0.32 M. Mercury(II) chloride (1.40 g, 5.25 mmol) in ether (5 ml) was added slowly to $(\text{Me}_3\text{Si})_2\text{CMeLi}$ (10.5 mmol) in ether (50 ml) and the mixture heated under reflux for 3 h. After hydrolysis with N sulphuric acid, the organic layer was separated and dried. Solvent and $(\text{Me}_3\text{Si})_2\text{CHMe}$ were distilled away leaving $[(\text{Me}_3\text{Si})_2\text{CMe}]_2\text{Hg}$. Yield 1 g, 34%. (Found: C, 34.2; H, 7.6. $\text{C}_{16}\text{H}_{42}\text{HgSi}_4$ calcd.: C, 35.0; H, 7.7%.) NMR: τ 9.56 (Me_3Si), 9.70 (Me). The mass spectrum showed a strong peak at m/e 533, corresponding to loss of methyl from the parent ion; apart from Hg^+ there was no other prominent mercury-containing species.

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