

Journal of Organometallic Chemistry, 193 (1980) 21–29
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CARBON-13 AND PROTON NMR PARAMETERS OF NEOPENTYL- AND TRIMETHYLSILYLMETHYL-THALLIUM(III) DERIVATIVES AND THE X-RAY CRYSTAL STRUCTURE OF BIS(TRIMETHYLSILYLMETHYL)CHLOROTHALLIUM(III)

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(Received January 8th, 1980)

Summary

Carbon-13 and proton NMR spectra have been determined for organothallium(III) derivatives of the types $RTlX_2$ and R_2TlX ($R = (CH_3)_3CCH_2$ or $(CH_3)_3SiCH_2$; $X = Cl, Br$ or $O_2CCH(CH_3)_2$). The dependence of coupling of ^{13}C and 1H to thallium on the number and nature of R groups is discussed in terms of the Fermi contact mechanism for spin–spin coupling.

The crystal structure of $[(CH_3)_3SiCH_2]_2TlCl$ has been determined. The compound crystallises in the monoclinic space group $P2_1/n$, with a 10.618, b 24.492, c 6.017 Å, β 99.76°. The molecule is dimeric with each four-coordinate thallium atom bonded unequally to two bridging chlorine atoms. The C–Tl–C angle is 168°.

Introduction

As part of a detailed study of NMR parameters of organothallium compounds [1–3] we have determined ^{13}C and 1H NMR spectra for neopentyl- and trimethylsilylmethyl-thallium(III) derivatives of the types $RTlX_2$ and R_2TlX ($X = \text{anion}$). We report here the dependence of chemical shift and coupling to thallium on silicon substitution, on the number of alkyl groups attached to thallium, and on the position of coupled C and H atoms in the alkyl groups. Proton NMR spectra have previously been determined for a wide variety of alkylthallium(III) compounds [4] but reports of ^{13}C NMR parameters have been limited to methyl derivatives [1–6].

Molecular weight determinations [7] indicate that $[(\text{CH}_3)_3\text{CCH}_2]_2\text{TlCl}$ and $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{TlCl}$ are dimeric in CHCl_3 solution and the IR spectra of the trimethylsilylmethyl compound suggest that the C—Tl—C unit is bent in the solid state and in solution [8]. The single crystal X-ray structure of $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{TlCl}$ has been determined in order to confirm the dimer formulation and quantify the geometry of the C—Tl—C unit.

Experimental

Preparation of bis(trimethylsilylmethyl)chlorothallium(III). This compound was previously prepared by reaction of lithiomethyltrimethylsilane with thallium(III) chloride [7,8]. The Grignard reagent was employed in the present work. A solution of trimethylsilylmethylmagnesium chloride [9], prepared from trimethylsilylmethylchloride (20.2 g; 0.16 mol) and magnesium (4.0 g; 0.17 mol) in dry diethyl ether (75 cm³), was cooled to -15°C . Thallium(III) chloride [10] (18.5 g; 0.06 mol) in dry Et_2O was added with stirring during 1 h. The reaction mixture was allowed to warm to room temperature and stirred for a further 2.5 h. Hydrolysis with aqueous ammonium chloride solution, followed by stirring for 0.5 h and subsequent filtration, gave 25.8 g of crude product. Recrystallization from chloroform gave colourless needles suitable for single crystal X-ray analysis. (Found: C, 23.3; H, 5.3. $\text{C}_8\text{H}_{22}\text{Si}_2\text{TlCl}$ calcd.: C, 23.2; H, 5.3%).

Preparation of bis(trimethylsilylmethyl)isobutyrate thallium(III) [7,8]. This was prepared by refluxing (3 h) equimolar amounts of bis(trimethylsilylmethyl)chlorothallium(III) and isobutyrate silver(I) in methanol. Filtration, evaporation and subsequent recrystallization from methanol gave the product as colourless needles. (Found: C, 30.9; H, 5.9. $\text{C}_{12}\text{H}_{29}\text{O}_2\text{Si}_2\text{Tl}$ calcd.: C, 30.9; H, 6.2%.)

Preparation of trimethylsilylmethylbis(isobutyrate)thallium(III). This was prepared as previously reported [7]. (Found: C, 30.9; H, 5.4. $\text{C}_{12}\text{H}_{25}\text{O}_4\text{SiTl}$ calcd.: C, 30.9; H, 5.4%.) ¹H and ¹³C NMR spectra showed the presence of a small amount of impurity.

Preparation of bis(neopentyl)chlorothallium(III) [7]. This compound was prepared from neopentylchloride and thallium(III) chloride in a similar way to that described above for the trimethylsilylmethyl analogue. Recrystallisation from pyridine gave colourless needles. (Found: C, 31.6; H, 5.7. $\text{C}_{10}\text{H}_{22}\text{TlCl}$ calcd.: C, 31.4; H, 5.8%.)

Preparation of bis(neopentyl)isobutyrate thallium(III). This compound was prepared by an analogous method to that described above for the trimethylsilylmethyl derivative. (Found: C, 38.8; H, 6.7. $\text{C}_{14}\text{H}_{29}\text{TlO}_2$ calcd.: C, 38.8; H, 6.7%.)

Preparation of neopentylbis(halo)thallium(III) [11]. Equimolar amounts of bis(neopentyl)chlorothallium(III) and pyridinium perbromide were reacted in CH_2Cl_2 [11]. Evaporation to low bulk followed by filtration and evaporation of the filtrate to dryness gave a pale green solid which was washed with pet. ether and dried under vacuum. ¹H NMR spectra of the products of a number of separate preparations indicated the presence of some R_2TlX impurity (up to ca. 30%).

Preparation of neopentylbis(isobutyrate)thallium(III). This compound was prepared in situ in an NMR tube by a similar method to that reported [7] for the analogous trimethylsilylmethyl compound. ^1H NMR indicated that the reaction proceeded to ca. 60% completion.

Microanalyses were carried out by the Butterworth Microanalytical Service.

NMR Spectra

Proton spectra were recorded on a Perkin Elmer R12B NMR spectrometer at 60 MHz using internal TMS lock and a frequency counter for measurement of signal positions. Assignments were generally obvious. In some cases pairing of components arising from $^{205}\text{Tl}-^1\text{H}$ spin-spin coupling was confirmed by double resonance experiments using the general nuclear Overhauser effect [12].

Carbon-13 spectra were obtained at 22.63 MHz and 45.28 MHz on Bruker HX 90E and WH180 spectrometers respectively. Relative signs of $^1J(\text{Tl}-\text{C})$ and $^2J(\text{Tl}-\text{H})$ in bis(neopentyl)chlorothallium(III) were obtained by selective $^{13}\text{C}-\{^1\text{H}\}$ experiments. Assignments of broad band $^{13}\text{C}-\{^1\text{H}\}$ spectra were unambiguous except for trimethylsilylmethylbis(isobutyrate)thallium(III) which was assigned by comparison with the coupled spectrum. Spectra were referenced to internal TMS and the deuterium resonance of the solvent was used as lock.

Crystallography

Measurements were made on a Philips PW1100 four circle diffractometer with graphite monochromated Mo- K_{α} radiation (λ 0.7107 Å). Crystal data are given in Table 1, together with other experimental details. The structure was solved using standard Patterson methods with SHELX76 [13]. The molecular

TABLE 1
CRYSTAL DATA AND EXPERIMENTAL DETAILS FOR $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{TlCl}\}_2$

| Crystal system | Monoclinic | Crystal size (mm) | 0.29 × 0.16 × 0.13 |
|---|---|----------------------------------|--|
| Space group | $P2_1/n$ | Scan method | $\theta-2\theta$, $0.05^\circ \text{ s}^{-1}$ in θ ; scan and total background count durations equal. |
| a (Å) | 10.618 (3) | Maximum $\sin \theta/\lambda$ | 0.597 Å $^{-1}$ |
| b (Å) | 24.492 (5) | Absorption correction | Semi-empirical based on a pseudo-ellipsoid model and 449 azimuthal scans from 33 reflections [15] |
| c (Å) | 6.017 (2) | | |
| β (°) | 99.76 (3) | | |
| V (Å 3) | 1542.1 (23) | | |
| Z | 4 | Atomic scattering factors | International Tables for X-ray crystallography (1974) |
| $F(000)$ | 784 | | |
| $\mu(\text{Mo}-K_{\alpha})(\text{mm}^{-1})$ | 10.342 | No. reflections $F > 6\sigma(F)$ | 1703 |
| Formula weight | 414 | No. parameters | 71 |
| Weighting scheme, w | 2.8137/ $[\sigma^2(F^2) + 3.81 \times 10^{-4}F^2]$ | Refinement scheme | Full matrix on F |
| Final R factors | | Standard reflections | Measured every 6 h; showed a decrease of 13% during data collection and were used to scale the data to a common level. |
| R_F | 0.080 | | |
| R_w | 0.087 | | |

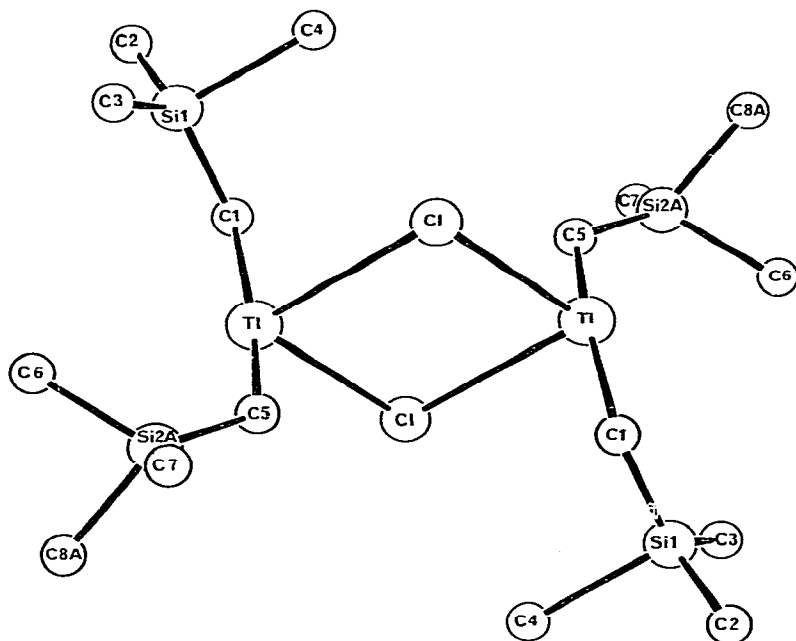


Fig. 1. The structure of $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{TiCl}\}_2$. The disorder in the trimethylsilylmethyl groups is not shown.

structure and labelling scheme are shown in Fig. 1 (ORTEP2 [14]). The structure displays disorder in one of the $(\text{CH}_3)_3\text{Si}$ groups (Fig. 2). Two equal positions for atoms Si(2) and C(8) were found. A tetrahedral model involving geometric constraints to the disordered Si atom was used in the refinement. The refined parameters included anisotropic thermal parameters for Ti, Cl, Si(1).

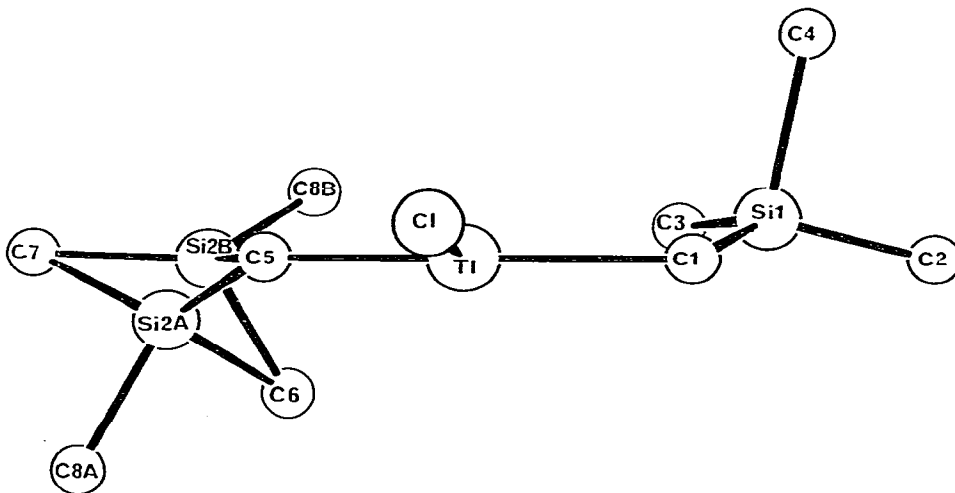


Fig. 2. The structure of a monomer unit of $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{TiCl}\}_2$ showing disorder in the trimethylsilylmethyl group.

TABLE 2

FINAL FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $\{[(\text{CH}_3)_3\text{SiCH}_2\text{I}_2\text{TlCl}]\}_2^a$

| Atom | x | y | z |
|--------|-----------|----------|------------|
| Tl | 0464(1) | 0591(1) | 2615(2) |
| C(1) | -1442(36) | 0976(15) | 2172(61) |
| C(2) | -3011(57) | 2032(25) | 1777(99) |
| C(3) | -0157(75) | 1989(31) | 0266(129) |
| C(4) | -2608(96) | 1491(40) | -2002(169) |
| C(5) | 2477(32) | 0383(13) | 3201(55) |
| C(6) | 3281(42) | 1389(19) | 5236(76) |
| C(7) | 5283(53) | 0791(22) | 3044(90) |
| C(8A) | 4654(80) | 0612(34) | 7080(130) |
| C(8B) | 3093(83) | 1565(38) | 1324(141) |
| Si(1) | -1544(11) | 1680(4) | 1167(17) |
| Si(2A) | 3769(22) | 0722(9) | 4161(39) |
| Si(2B) | 3530(23) | 0919(10) | 2899(41) |
| Cl | -0382(11) | -0477(3) | 2362(12) |

^a E.s.d.'s in parentheses.

The final atomic coordinates for the atoms are listed in Table 2. Due to the disordered nature of the crystals, a detailed analysis of the molecular bonding parameters within the $(\text{CH}_3)_3\text{Si}$ group was not possible. Hydrogen atom positions were not found. Interatomic distances and angles involving thallium are given in Table 3. Complete tables of interatomic distances, angles, and thermal parameters, and lists of observed and calculated structure factors are available from the authors.

Results and discussion

NMR spectra

Carbon-13 and proton NMR parameters, respectively, are given in Tables 4 and 5 for the neopentylthallium(III) derivatives, $[(\text{CH}_3)_3\text{CCH}_2]_n\text{TlX}_{3-n}$, and the trimethylsilylmethylthallium(III) derivatives $[(\text{CH}_3)_3\text{SiCH}_2]_n\text{TlX}_{3-n}$, ($n = 1, 2$; X = anion). The previously reported proton NMR parameters for bis-(neopentyl)chlorothallium(III) and neopentyl-dihalothallium(III) in pyridine

TABLE 3

INTERATOMIC DISTANCES AND ANGLES INVOLVING THALLIUM FOR $\{[(\text{CH}_3)_3\text{SiCH}_2\text{I}_2\text{TlCl}]\}_2^a$

| Distances ^b | | | |
|------------------------|---------|--------------------------|----------|
| Tl—C(1) | 2.21(4) | Tl—Cl ⁱ | 2.99(1) |
| Tl—Cl | 2.76(1) | Tl . . . Tl ⁱ | 4.308(2) |
| Tl—C(5) | 2.17(3) | Cl . . . Cl ⁱ | 3.87(2) |
| Angles ^c | | | |
| C(1)—Tl—C(5) | 168(1) | Tl—Cl—Tl ⁱ | 96(1) |
| C(1)—Tl—Cl | 97(1) | C(1)—Tl—Cl ⁱ | 92(1) |
| C(5)—Tl—Cl | 95(1) | C(5)—Tl—Cl ⁱ | 91(1) |
| Cl—Tl—Cl ⁱ | 84(1) | | |

^a The superscript i refers to the symmetry transformation $-x, -y, 1 - z$. E.s.d.'s in parentheses. ^b In Å.^c In degrees.

TABLE 4

¹³C NMR PARAMETERS FOR NEOPENTYL- AND TRIMETHYLSILYLMETHYL-THALLIUM(III) DERIVATIVES ^a

| Compound | Solvent ^b | Conc. ^c | ¹ J(Tl—C) ^{d,e} (δC) ^f | ² J(Tl—C) ^{d,g} (δC) ^f | ³ J(Tl—C) ^{d,g} (δC) ^f |
|---|-----------------------------------|--------------------|--|--|--|
| [(CH ₃) ₃ CCH ₂] ₂ TlCl | Pyridine | 0.4 | ±2297 (67.5) | 26 (33.2) | 310 (34.4) |
| (CH ₃) ₃ CCH ₂ TlX ₂ ^h | Pyridine | 0.1 | 5002 (63.4) | 313 (34.3) | 640 (32.4) |
| [(CH ₃) ₃ SiCH ₂] ₂ TlCl | Pyridine | 0.2 | 1847 (30.6) | — | 168 (5.5) |
| [(CH ₃) ₃ SiCH ₂] ₂ Tl- OCOCH(CH ₃) ₂ | Pyridine | 0.3 | 1940 (28.7) | — | 168 (1.8) |
| (CH ₃) ₃ SiCH ₂ Tl- [OCOCH(CH ₃) ₂] ₂ | Dichloro- methane ^j | 0.1 ^m | 3540 ^{g,h} (27.2) ⁱ | — | 318 (-1.1) |

^a At 18 ± 1°C. ^b Deuterated solvents were used unless otherwise noted. ^c In mol dm⁻³. ^d In Hz (±3). ^e ^J(²⁰⁵Tl—C) unless otherwise noted. ^f In ppm relative to internal TMS; error ± 0.13 ppm. ^g Separate coupling to ²⁰³Tl and ²⁰⁵Tl not resolved. ^h Error ± 30 Hz. ⁱ Error ± 0.45 ppm. ^j CH₂Cl₂/CD₂Cl₂. ^k X = Cl and/or Br. ^m Approximate concentration.

solution [11] are in good agreement with the present work, with the exception of ²J(Tl—H) for (CH₃)₃CCH₂TlX₂ (X = Cl and/or Br) for which the value of 712 Hz was given. Previous values [8] of ²J(Tl—H) for R₂TlCl and R_nTl-[OCOCH(CH₃)₂]_{3-n} in CDCl₃ (R = (CH₃)₃SiCH₂, n = 1,2) also agree closely with the values reported here.

The largest changes in ¹³C and ¹H chemical shifts within the organothallium groups are caused by substitution of silicon for carbon. This results in increases in the shielding of CH₂ and CH₃ carbon atoms by ca. 30 ppm and protons by ca. 1 ppm. Variations in δ(¹³C) and δ(¹H) with anion, solvent, and the number of groups attached to Tl are generally smaller (<5 ppm for ¹³C; <0.9 ppm for ¹H).

The thallium—carbon and thallium—proton coupling constants decrease from RTlX₂ to R₂TlX derivatives. This is in agreement with previous ¹H and ¹³C NMR studies of organothallium(III) derivatives which support the assumption that the Fermi contact mechanism is the dominant contribution to the coupling [2, and references therein]. ¹J(Tl—C) is expected to be proportional to (Z_{eff})³ · α²(Tl) [2] giving a ratio of 1 : 2.2 for the values of ¹J(Tl—C) for R₂TlX : RTlX₂ under similar conditions of anion and solvent. The ¹J(Tl—C) ratios for the neopentyl and trimethylsilylmethyl derivatives are 1 : 2.2 and 1 : 1.8, respectively. The ratios of coupling constants between non-directly bonded atoms might also be expected to have similar values, though with less justification [2]. The ratios involving ³J(Tl—C), ²J(Tl—H) and ⁴J(Tl—H) are all close to 1 : 2, but interestingly the ratio for ²J(Tl—C) in the neopentyl derivatives is considerably different (1 : 12).

Substitution of Si for C in otherwise similar compounds causes considerable decreases in ¹J(Tl—C) (450 and 1462 Hz for dialkyl and monoalkyl compounds, respectively). Large reductions in ¹J(¹⁹⁹Hg—C) on silicon substitution have also been noted for neopentyl and trimethylsilylmethyl derivatives of the types R₂Hg and RHgCl [16–19]. These changes may be rationalised on the

TABLE 5
 PROTON NMR PARAMETERS FOR NEOPENTYL- AND TRIMETHYLSILYLMETHYL-THALLIUM(III)
 DERIVATIVES ^a

| Compound | Solvent ^b | Conc. ^c | ² J(Tl-H) ^d (δH) ^e | ⁴ J(Tl-H) ^d (δH) ^e |
|---|----------------------|--------------------|--|--|
| [(CH ₃) ₃ CCH ₂] ₂ TlCl | Pyridine | 0.21 | 7415 (2.38) | 31 (1.09) |
| | Benzene | 0.02 | 394 ^f (2.61) | 31 (1.03) |
| | Chloroform | 0.14 | 388 (2.47) | 31 (1.11) |
| [(CH ₃) ₃ CCH ₂] ₂ TlOCOCH(CH ₃) ₂ ^h | Pyridine | 0.23 | 429 (2.19) | 31 (1.10) |
| | Benzene | 0.18 | 422 (2.23) | 31 (1.09) |
| | Chloroform | 0.26 | 411 (2.07) | 31 (1.08) |
| (CH ₃) ₃ CCH ₂ TlX ₂ ^j | Pyridine | <i>i</i> | 665 (2.74) | 68 (1.15) |
| | Chloroform | <i>i</i> | 666 ^g (2.92) | 73 (1.17) |
| (CH ₃) ₃ CCH ₂ Tl[OCOCH(CH ₃) ₂] ₂ ^h | Chloroform | <i>i</i> | 772 ^g (2.90) | 75 (1.14) |
| [(CH ₃) ₃ SiCH ₂] ₂ TlCl | Pyridine | 0.22 | 556 (1.27) | 18 (0.16) |
| | Chloroform | 0.04 | 541 (1.39) | 17 (0.15) |
| | DMSO | 0.05 | 592 (0.83) | 18 (0.08) |
| [(CH ₃) ₃ SiCH ₂] ₂ TlOCOCH(CH ₃) ₂ ^h | Pyridine | 0.27 | 563 (1.07) | 18 (0.17) |
| | Chloroform | 0.08 | 554 (1.09) | 18 (0.11) |
| | Methanol | 0.03 | 571 (0.95) | 17 (0.11) |
| (CH ₃) ₃ SiCH ₂ Tl[OCOCH(CH ₃) ₂] ₂ ^h | Pyridine | 0.10 ^k | 1116 (1.71) | 33 (0.17) |
| | Chloroform | 0.10 ^k | 1130 ^g (1.76) | 31 ^g (0.20) |

^a At 35 ± 1°C. ^b Deuterated solvents. ^c In mol dm⁻³. ^d In Hz. Error ± 1 Hz unless otherwise noted. ^e In ppm relative to internal TMS; error ± 0.02 ppm unless otherwise noted. ^f Errors: *J*, ±3 Hz; *δ*, ±0.05 ppm. ^g Errors: *J*, ±4 Hz; *δ*, ±0.05 ppm. ^h Protons in the isobutyrate anion are not coupled to thallium. ⁱ Reaction carried out in NMR tube and product not isolated. Conc. ca. 0.1 mol. dm⁻¹. ^j X = Cl and/or Br. ^k Approximate concentration.

basis of Bent's postulate [20] that the *s*-character of an atom tends to concentrate in orbitals directed towards the more electropositive substituents. For the Fermi contact mechanism, the one-bond coupling constants in analogous neopentyl and trimethylsilylmethyl compounds will be proportional to the α²(C) term and this term will be decreased by substitution of silicon for the β-carbon. ³J(Tl-C) and ⁴J(Tl-H) are also reduced by about half by silicon substitution. In contrast, ²J(Tl-H) is increased by 134–207 Hz for R₂TlX compounds and by 358 Hz for RTl(OCOCH(CH₃)₂)₂ compounds. Broadly similar

results were observed for the analogous mercury compounds [16,17,19,21,22]. ^{13}C - $\{^1\text{H}\}$ experiments for $[(\text{CH}_3)_3\text{CCH}_2]_2\text{TlCl}$ in pyridine solution show that the signs of $^1J(\text{Tl}-\text{C})$ and $^2J(\text{Tl}-\text{H})$ are opposite, and it is reasonable to suppose that similar sign combinations are present in the other neopentyl and trimethylsilylmethyl compounds studied. The dependence of the coupling constants on anion and solvent are small compared to the effect of Si substitution and of changing the number of organo-groups on thallium.

Crystal structure of $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{TlCl}\}_2$

Kurosawa et al. [7,8] proposed, on the basis of IR and molecular weight studies, that bis(trimethylsilylmethyl)chlorothallium(III) is dimeric in the solid state and in chloroform solution and contains a bent C—Tl—C configuration. The structure determined here confirms the dimer formulation but shows the C—Tl—C unit to be close to linear.

The structure consists of centrosymmetric dimers $\{[(\text{CH}_3)_3\text{SiCH}_2]_2\text{TlCl}\}_2$ with each thallium atom bonded unequally to the two bridging chlorine atoms. Further association to form polymeric chains would be expected to occur through chlorine bridges. However the shortest interdimer Tl—Cl distances found are Tl ... Clⁱⁱ, 10.95 Å; Tl ... Clⁱⁱⁱ, 12.91 Å (superscripts ii and iii refer to the symmetry transformations $1.5 - x, \frac{1}{2} + y, 1.5 - z$ and $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ respectively). The shortest interdimer Tl ... Tl distances are Tl ... Tlⁱⁱ, 12.99 Å and Tl ... Tlⁱⁱⁱ, 10.92 Å.

The thallium atom is four-coordinate with a coordination geometry based on a distorted trigonal bipyramid with one equatorial position vacant and both axial Tl—C bonds slightly bent towards the vacant position. The C—Tl—C angle ($168(1)^\circ$) is within the range (163 – 180°) previously reported [3,23] for $(\text{alkyl})_2\text{TlX}$ derivatives (X = uninegative anion).

Acknowledgements

We thank the S.R.C. for financial support for purchase of X-ray diffractometer equipment, for use of the PCMU ^{13}C NMR facility, and for a Research Studentship (to F.B.). We thank Dr. M. McPartlin for her interest in this work.

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