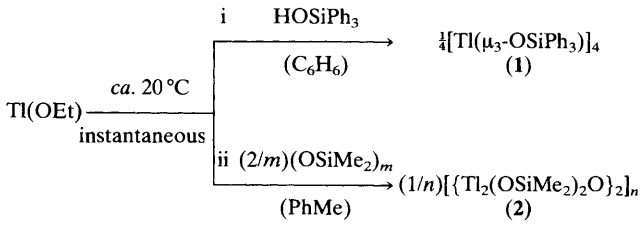
Conversion of the Silicone Poly(dimethylsiloxane) by Thallium(I) Ethoxide into the Ladder Polymer $[\{Tl_2(OSiMe_2)O\}_2]_n$; *X*-Ray Structure of the Product and of Thallium(I) Triphenylsilanolate†

Stephen Harvey,[a] Michael F. Lappert,[b] Colin L. Raston,[a] Brian W. Skelton,[a] Ghanshyam Srivastava,[b] and Allan H. White[a]

[a] *Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia*
[b] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.*

Treating silicone grease $(OSiMe_2)_m$ with an excess of TlOEt in PhMe at ambient temperature instantly yields the poly(thalliodimethylsiloxane) $[\{Tl_2(OSiMe_2)_2O\}_2]_n$ which, like $[Tl(\mu_3\text{-}OSiPh_3)]_4$ (obtained similarly from the ethoxide and $HOSiPh_3$), has been characterised by *X*-ray crystallography; both structures contain Tl_4O_4 cuboids [Tl–O distances and O–Tl–O angles are in the range 2.48(2)—2.78(2) Å and 75.4(5)—84.8(6)°].

This communication contributes to two areas: that of thallium(I) alkoxides and of the organic poly(metallosiloxanes) (for M = Tl^I). Thus, we report the synthesis (Scheme 1) and the *X*-ray structures of $[Tl(\mu_3\text{-}OSiPh_3)]_4$ (**1**) (Figure 1)‡ and the ladder polymer $[\{Tl_2(OSiMe_2)_2O\}_2]_n$ (**2**) (Figure 2),‡ both of which contain Tl_4O_4 cuboids.



Scheme 1

Although Tl^I alkoxides have been known for more than a century[1] and the commercially available TlOEt is becoming a convenient precursor of other Tl^I complexes (*e.g.*[2] cyclopentadienyls), 'hard' structural data are scarce. Because (i) several homologues are tetramers in solution [including $Tl(OEMe_3)$ (E = C or Si) in benzene (cryoscopy)[3]] and (ii) a (largely) two-dimensional *X*-ray structural study of crystalline TlOMe showed that the Tl atoms are positioned at the vertices of a regular tetrahedron (no other atoms were located; the crystals decomposed under Mo-K_α radiation),[4] it is often assumed[5] that Tl^I alkoxides have cubane structures, like those of the isoleptic alkali metal (K, Rb, or Cs) t-butoxides.[6]

Colourless crystals of compounds (**1**) and (**2**) (satisfactory microanalytical data were obtained) were prepared from thallium(I) ethoxide under ambient conditions (Scheme 1). The thallium(I) triphenylsilanolate (**1**) was precipitated in high yield after transesterification in benzene (i in Scheme 1) and was recrystallised (C_6H_6–C_5H_{12}) to give the benzene solvate $[Tl(\mu_3\text{-}OSiPh_3)]_4.C_6H_6$. More surprisingly, poly(dimethylsiloxane) (in the form of silicone grease) rapidly reacted with TlOEt in toluene, affording after *ca.* 12 h at −30 °C crystalline poly(thalliodimethylsiloxane) (**2**) (ii in Scheme 1), albeit in low yield; it is only sparingly soluble in aliphatic or aromatic hydrocarbons.

We suggest that each of these reactions proceeds by nucleophilic attack of $\bar{O}Et$ at a silicon atom of $HOSiPh_3$ or $(OSiMe_2)_n$. The degradation of a silicone to a disiloxane (ii in Scheme 1) is noteworthy and may have some potential; for example, reaction of $Al(OEt)_3$ (rather than TlOEt) with poly(dimethylsiloxane) may provide characterisable organic poly(aluminosiloxanes). The aluminosilicates are key inorganic poly(metallosiloxanes), but analogues having pendant organic groups remain ill defined. They gained some prominence in the 1950s from Andrianov's claims that they constituted a unique class of polymers, being organic solvent-soluble but infusible; an example was said to have the composition $[Al(OSiMe_3)(OSiMe_2)O]_n$, obtained by cocondensation of $SiMe_2(OAc)_2$ with an equimolar portion of $Al(OPr^i)_2OSiMe_3$.[7]

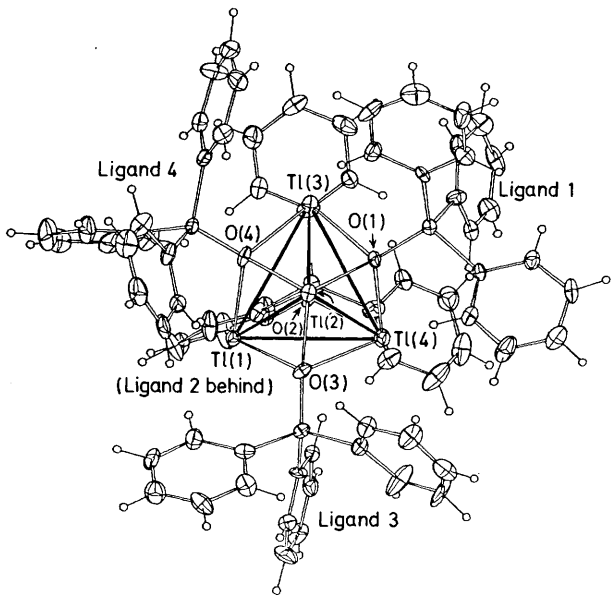


Figure 1. Molecular projection of $[Tl(\mu_3\text{-}OSiPh_3)]_4$ (**1**), showing 20% thermal ellipsoids for the non-hydrogen atoms; hydrogen atoms have arbitrary radii. Edges of the Tl_4 tetrahedron are shown as solid lines. Bond distances and angles range as follows: Tl–O 2.48(2)—2.78(2), Tl · · · Tl 3.798(2)—3.972(3), O–Si 1.61(2)—1.67(2) Å; O–Tl–O 78.3(6)—84.8(6), Tl–O–Tl 93.0(6)—103.6(5), Tl–O–Si 108.1(12)—129.2(9)°.

† No reprints available.

‡ *Crystal data*: (**1**), $(C_{18}H_{15}OSiTl)_4.C_6H_6$ ($C_{78}H_{66}O_4Si_4Tl_4$), triclinic, $P\bar{1}$, a = 19.33(1), b = 15.79(1), c = 13.90(1) Å, α = 64.16(6), β = 70.67(5), γ = 73.65(6)°, Z shows 2 tetramers, D_c = 1.87 g cm^{-3}, 6392 'observed' reflections [$I > 3\sigma(I)$], $2\theta_{max}$ = 50°, R = 0.068, R' = 0.080.

(**2**) $C_4H_{12}O_3Si_2Tl_2$, orthorhombic, *Pbna*, a = 18.542(5), b = 14.010(6), c = 9.297(5) Å, Z = 8, D_c = 3.15 g cm^{-3}, 1315 'observed' reflections [$I > 3\sigma(I)$], $2\theta_{max}$ = 60°, R = 0.057, R' = 0.048 [Mo-K_α radiation, λ = 0.71069 Å, T = 295 K]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

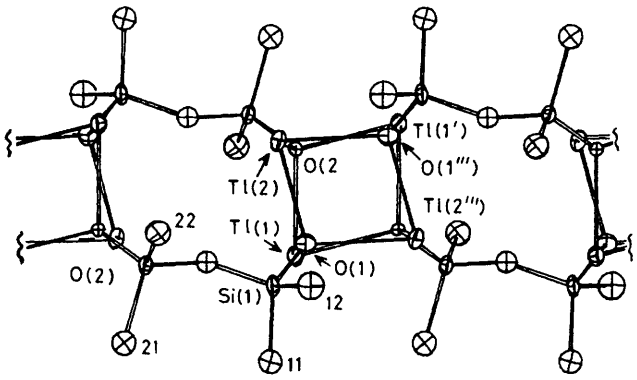


Figure 2. Projection of a section of a polymer strand of $[\{Tl_2(O\text{-}SiMe_2)_2O\}_2]_n$ (**2**), showng 20% thermal ellipsoids. Selected bond distances and angles are as follows: Tl–O 2.48(1)—2.59(2), Tl · · · Tl 3.798(2)—4.333(2), O(1,2)–Si(1,2) 1.62(2)—1.65(2) Å; O–Tl–O 75.4(4)—80.2(5), Tl–O–Tl 98.1(5)—104.2(5), Tl–O–Si 112.7(7)—121.8(10)°.

'Equilibration' of siloxanes is of considerable importance in the production of silicones; *e.g.* heating $O(SiMe_3)_2$ with an equimolar portion of $(OSiMe_2)_4$ at 80 °C in the presence of 0.1% $[NMe_4]OH$ yields a mixture of linear and cyclic polysiloxanes.[8]

Compounds (**1**) and (**2**) comprise tetrahedral arrays of thallium atoms with four oxygens centred over each triangular face, each approximately equidistant from three metal centres. Thus the structures have Tl_4O_4 cuboids (Figures 1 and 2). In (**1**), this and the associated $SiPh_3$ groups represent discrete tetranuclear species; in (**2**), two sets of diagonally opposite oxygen atoms are linked to two other such atoms of a neighbouring cuboid by way of $-Si(Me)_2OSi(Me)_2-$ bridges, so that the overall structure is that of a one-dimensional ladder polymer. Geometries within each of the Tl_4O_4 cuboids vary significantly but in no systematic fashion. A noteworthy difference between the two structures is the wider spread of Tl · · · Tl distances in (**2**). The disiloxane oxygen of the bridging ligand in (**2**) is not bound to the electrophilic three-co-ordinate thallium; this is consistent with the low Lewis basicity of silyl ethers, which have more open angles at oxygen than do organic ethers,[9] as is the case in (**2**) with the angle Si–O–Si = 148(1)°.

Each thallium site in (**1**) or (**2**) is pyramidal, with acute O–Tl–O angles, consistent with there being a stereochemically active lone pair of electrons associated with each Tl directed away from the centre of the cluster. The Tl–O distances, 2.48(2), 2.59(2) Å [in (**2**)] or to 2.78(2) Å [in (**1**)] are shorter than the sum of the ionic radii of Tl^+ and O^{2-} (2.88 Å),[10] reflecting some degree of covalent character in the Tl–O bonding. A similar bonding picture has recently been proposed for another *X*-ray-authenticated three-co-ordinate Tl^I complex, $[TIL][PF_6]$ (L = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane).[11]

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