Preparation and Crystal Structure of the Titanaspiro[7.7]heptasiloxane *cis*-Bis(Hexaphenyltrisiloxanediolato)dipyridine-titanium Bis(Toluene) Solvate

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The products isolated in good yield from the reactions of dilithium tetraphenyldisiloxanediolate [$Ph_4Si_2O(OLi)_2$] and (a) titanium tetrachloride (with subsequent addition of pyridine) or (b) dichloro(dimethyl)silane were the cyclic spiro[7.7]titanaheptasiloxane *cis*-$(Py)_2\overline{Ti(OSiPh_2[OSiPh_2]_2O})_2\cdot 2PhMe$ (**1**) and the cyclic tetrasiloxane $Me_2\overline{SiOSiPh_2[OSiPh_2]_2O}$ and not the expected titanadisiloxane (titanio-oxydisiloxane) and trisiloxane.

Ring strain energy in cyclic trisiloxanes is in the range 16—21 kJ mol^{-1}; those of higher molecular weight have virtually none. This is reflected in the fact that for a wide variety of bases, including alkali metal silanolates, the activation energy for the anionic polymerisation of cyclic trisiloxanes is about 11 kJ mol^{-1} lower than for those of greater ring size.[1] The isolation from our reactions of the titanaspiroheptasiloxane (**1**) rather than the expected titanadisiloxane may imply, as has been suggested for anionic polymerisation of cyclic trisiloxanes,[1] a ring expansion involving attack by silanolate ion on a silicon or the titanium atom in an intermediate strained titanatrisiloxane ring. Noteworthy in this respect is our observation that, when treated with dichloro(dimethyl)silane, $Ph_4Si_2O(OLi)_2$ gave the tetrasiloxane (**2**) rather than the trisiloxane.† However only the expected siloxane (**3**) was obtained from reactions between $Ph_4Si_2O(OLi)_2$ and trimethylchlorosilane. These experiments indicate that under the conditions employed for this work, expansion of the precursor siloxane chain occurs only when there is the possibility of cyclic trisiloxane formation. Andrianov's report[3] of the synthesis of the spiro complex $\overline{Ti(OSiPh_2OSiPh_2O})_2$[3] from the tetraphenyldisiloxanediol $Ph_4SiO_2(OH)_2$ and titanium tetrachloride in the presence of pyridine suggests that cyclic titaniodisiloxanes may be stable in the absence of strong base. Prior to this work the compound $\overline{Ti(OSiPh_2[OSiPh_2]_3O})_2$[4,5] was the only cyclic titanasiloxane structurally characterised.

$$Ph_4Si_2O(OLi)_2 + Me_2SiCl_2 \xrightarrow{THF, 0\,^{\circ}C} \underset{(\mathbf{2})}{Me_2\overline{Si[SiPh_2O]_3O}}$$

$$Ph_4Si_2O(OLi)_2 + 2Me_3SiCl \xrightarrow[-2LiCl]{THF, 0\,^{\circ}C} \underset{(\mathbf{3})}{Ph_4Si_2O(OSiMe_3)_2}$$

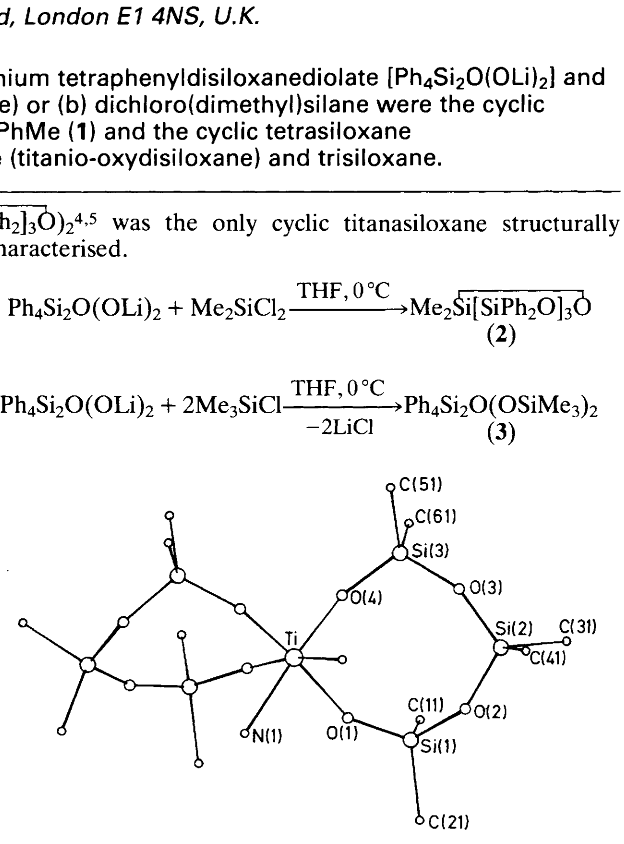

Figure 1. *X*-Ray crystal structure of *cis*-$(Py)_2Ti(OSiPh_2[OSiPh_2]_2O)_2\cdot 2PhMe$ (**1**) (toluene and phenyl groups, and pyridine carbon atoms omitted for clarity); selected bond lengths (Å) and angles (°): Ti–O(1) 1.873(5), Ti–O(4) 1.836(5), Ti–N(1) 2.291(6), O(1)–Ti–O(4) 95.5(2), O(4)–Ti–O(4) 102.5(3), N(1)–Ti–O(1) 83.7(2), N(1)–Ti–O(4) 168.6(2), N(1)–Ti–N(1) 79.7(3).

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† Compound (**2**) was previously prepared from treatment of the trisiloxanediol $Ph_6Si_3O_2(OH)_2$ with Me_2SiCl_2 in the presence of NH_3.[2]

Compound (**1**) was obtained when an ice-cooled dilute solution of titanium tetrachloride in tetrahydrofuran (THF) was treated with 2—3 equiv. of $Ph_4Si_2O(OLi)_2$ in THF. A concentrated toluene solution of the products was treated with pyridine and colourless cubic crystals of (**1**) were deposited at room temperature. The yield for the 1 : 3 molar ratio reaction was 52% (m.p. 97—100 °C).

The structure of (**1**) is given in Figure 1;‡ selected bond lengths and angles are listed in the caption. The most striking feature is the *cis*-disposition of the bulky chelating siloxanolato ligands and thus the chiral nature of the molecule. There is distorted octahedral geometry about the central titanium atom with the titanasiloxane rings adopting almost planar conformations. The Si–O(Si) bond lengths and Si–O–Si angles are close to those in the tetrahedral compound $\overline{\text{Ti}(\text{OSiPh}_2[\text{O-SiPh}_2]_3\text{O}})_2$.[5]

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‡ *Crystal data* for (**1**): $C_{96}H_{86}N_2O_8Si_6Ti$, M = 1612.236, monoclinic, a = 19.397(7), b = 17.369(5), c = 27.094(11) Å, β = 108.13(3)°, U = 9674.96 Å^3, space group $C_{2/c}$, Z = 4, D_c = 1.23 g cm^{-3}; $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å, μ = 1.98 cm^{-1}. Data recorded with CAD4 diffractometer in ω–2θ scan mode; 5309 unique reflections measured, 3432 observed with $[F > 3\sigma F_o]$. Structure solved by direct methods, refined by least-squares [phenyl groups treated as rigid hexagons (C–C 1.395 Å) with inclusion of hydrogen atoms at fixed distance (C–H 0.96 Å)] to R = 0.0595, R_w = 0.0586 for 438 parameters. 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, 1988.