Cyclic Metallasiloxane Compounds of Ti^{IV} and Zr^{IV}. *X*-Ray Crystal Structures of a *cis*-Bis(pyridine) Bis(cyclosiloxy)titanate and a Pyridinelithiated Tris(cyclosiloxy)zirconate†

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The reaction between $Si_2Ph_4O(OLi)_2$ (**1**) and $TiCl_4$ in 2:1 or 3:1 molar ratio gave on addition of pyridine (py) the titanatrisiloxane compound $[Ti\{OSiPh_2(OSiPh_2)_2O\}_2(py)_2]\cdot 2C_6H_5Me$ (**2**). Treatment of $ZrCl_4$ with (**1**) in 1:2 molar ratio gave the zirconadisiloxane system $Li_2Zr(OSiPh_2OSiPh_2O)_3]\cdot 3py\cdot 1.5C_6H_5Me$ (**3**). Compound (**2**) was also isolated from reactions employing the diol $Si_2Ph_4O(OH)_2$ and $TiCl_4$ in 2:1 molar ratio in the presence of pyridine. Siloxane chain expansion was also observed in the product from reaction of (**1**) with $SiMe_2Cl_2$ but not from reaction with $SiMe_3Cl$. The formation of the cyclic titanatrisiloxane and the cyclic tetrasiloxane is presumably a consequence of the ring strain in the titanadisiloxane and trisiloxane systems respectively, rather than a tendency of the siloxanediolate species (**1**) to oligomerise in the presence of base or metal halides. Compounds (**2**) and (**3**) have been studied by *X*-ray crystallography.

Cyclic siloxane systems, important intermediates in the production of silicones, have been thoroughly investigated,[1] but little is known of related cyclic metallasiloxanes. We have recently reported[2] on the isolation of the compound *cis*-$[Ti\{OSiPh_2(OSiPh_2)_2O\}_2(py)_2]$ (**2**) (py = pyridine) from the reaction between $TiCl_4$ and $Si_2Ph_4O(OLi)_2$ (**1**). We have now carried out the reaction between compound (**1**) and $ZrCl_4$ under conditions similar to those used for the titanium reaction. The product was shown by crystallography to be the essentially octahedral zirconadisiloxane tris chelate system, $Li_2[Zr(OSiPh_2OSiPh_2O)_3]\cdot 3py$ (**3**). Chain expansion of the siloxane as found in the reaction with $TiCl_4$ was not observed in the case of zirconium. The chemistry described in this paper is summarised in the Scheme.

Results and Discussion

Compounds (**2**)—(**5**), Table 1, represent the few reported examples of well characterised cyclic metallasiloxanes of the Group 4 transition metals. The mode of formation of the oligomeric metallasiloxanes (**4**)[3] and (**5**)[4] was not clear but must involve condensation of the precursor silanediol. Compounds (**2**) and (**3**) were prepared by treatment of the metal halides in tetrahydrofuran (thf) at 0 °C with $Si_2Ph_4O(OLi)_2$ in thf in 1:2 or 1:3 and 1:2 molar ratios respectively. When pyridine was added to concentrated toluene solutions of the products and these mixtures heated until clear solutions were obtained and allowed to cool slowly, colourless cubic, apparently air-stable crystals of (**2**) and (**3**) were obtained. The apparently low 'melting point' of the titanium compound was probably due to the release of co-ordinated pyridine. Similar features were observed in the i.r. spectra of the two species, the main differences being that bands, tentatively assigned to Si–O–Si stretching, in the region 1 120—1 010 cm^{-1} (see Experimental section for data), were less defined and at slightly higher wavenumbers for the titanium compound. The two different chemical environments of silicon in compound (**2**) were distinguished by ^{29}Si n.m.r. spectroscopy with the resonance due to the silicon distal to titanium occurring at slightly higher field. The ^{29}Si n.m.r. spectrum for compound (**3**) consisted of a single resonance, probably indicating rapid exchange of the bridging lithiums. This was supported by the observation of a single resonance in the ^{7}Li n.m.r. spectrum of (**3**). The pyridine-promoted dehydrochlorination reaction as shown in equation (1) was reported to give compound (**6**) in 14% yield.[5] We have

Table 1. Cyclic metallasiloxanes of Ti, Zr, and Hf

Compound	Reagents (relative molar quantities)	Ref.
(**2**) *cis*-$[Ti\{OSiPh_2(OSiPh_2)_2O\}_2(py)_2]$	$TiCl_4$, $Si_2Ph_4O(OLi)_2$, py (1:2 or :3, excess)	*a*
(**3**) $Li_2[Zr(OSiPh_2OSiPh_2O)_3]\cdot 3py$	$ZrCl_4$, $Si_2Ph_4O(OLi)_2$, py (1:2, exess)	*a*
(**4**) $[NEt_2H_2]_2[M(OSiPh_2OSiPh_2O)_3]$ M = Zr or Hf	$M(NEt_2)_4$, $SiPh_2(OH)_2$ (1:6)	3
(**5**) $[Ti\{OSiPh_2(OSiPh_2)_3O\}_2]$	$Ti(OPr^i)_4$, $SiPh_2(OH)_2$ (1:8)	4
(**6**) $[Ti(OSiPh_2OSiPh_2O)_2]$	$TiCl_4$, $Si_2Ph_4O(OH)_2$, py (1:2:4)	5
(**7**) $[Zr(Si_7O_{12})(C_5Me_5)(C_6H_{11})_7]$	$Zr(C_5Me_5)(CH_2Ph)_3$, $Si_7(C_6H_{11})_7O_9(OH)_3$ (1:1)	*b*

[a] This work. [b] F. J Feher, *J. Am. Chem. Soc.*, 1986, **108**, 3850.

$$TiCl_4 + Si_2Ph_4O(OH)_2 \longrightarrow \underset{(\mathbf{6})}{[Ti(OSiPh_2OSiPh_2O)_2]} \qquad (1)$$

found that when this material‡ isolated as described[5] was treated with toluene–pyridine mixtures, compound (**2**) and not the pyridine adduct of (**6**) was obtained. Furthermore examination of the remaining crude products from reaction (1) revealed the presence of the titanatrisiloxane (**2**). The apparently facile

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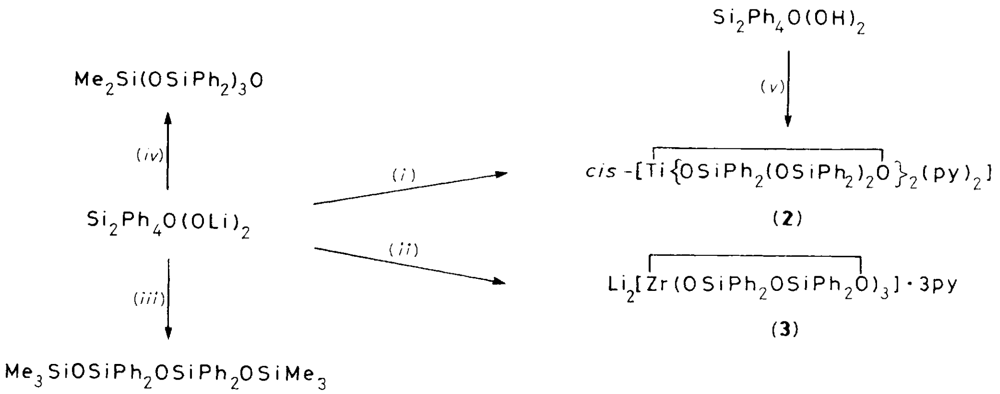
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

‡ Satisfactory elemental analysis for compound (**6**) was obtained by these authors[5] and us but no further evidence for this structure is available.



Scheme. (*i*) $TiCl_4$ and (**1**) in 1:2 or 1:3 molar ratio, thf, 0 °C, crystals from toluene–pyridine; (*ii*) $ZrCl_4$ and (**1**) in 1:2 molar ratio, thf, 0 °C, crystals from toluene–pyridine; (*iii*) $SiMe_3Cl$ and (**1**) in 2:1 molar ratio, thf, 0 °C, crystals from pentane; (*iv*) $SiMe_2Cl_2$ and (**1**) in 1:1 molar ratio, thf, 0 °C, crystals from pentane; (*v*) as described[5] with subsequent addition of excess of pyridine

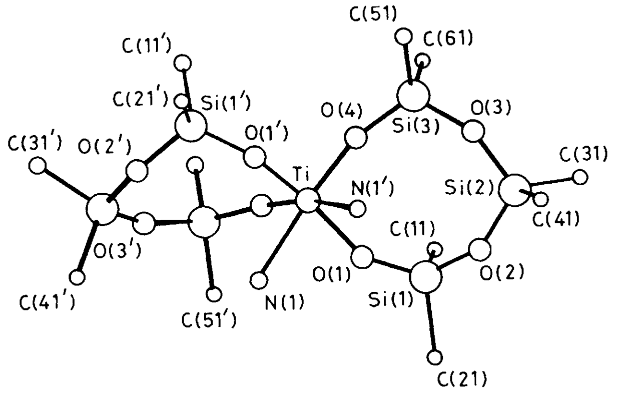


Figure 1. The molecular structure of *cis*-$[\overline{Ti\{OSiPh_2(OSiPh_2)_2O}\}_2(py)_2]\cdot 2C_6H_5Me$ (**2**) (phenyl groups and pyridine carbon atoms omitted for clarity)

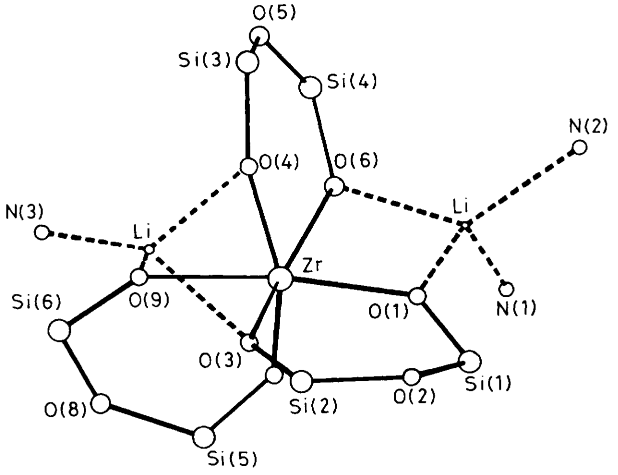


Figure 2. The molecular structure of $Li_2[\overline{Zr(OSiPh_2OSiPh_2O})_3]\cdot 3py\cdot 1.5C_6H_5Me$ (phenyl groups and pyridine carbon atoms omitted for clarity)

formation of cyclic titanatrisiloxanes from these reactions is probably promoted by ring strain in the cyclic titanadisiloxane system. The precursor silanolate did not undergo chain expansion in reactions with chlorotrimethylsilane. The mass spectrum of the product was consistent with the formation of the hexamethyltetraphenyltetrasiloxane compound as shown in the Scheme.

Table 2. Bond lengths (Å) and angles (°) for compound (**2**)

O(1)–Ti	1.874(5)	O(4)–Ti	1.836(5)
N(1)–Ti	2.285(6)	O(1)–Si(1)	1.603(5)
O(2)–Si(1)	1.630(6)	C(11)–Si(1)	1.874(6)
C(21)–Si(1)	1.872(7)	O(2)–Si(2)	1.623(6)
O(3)–Si(2)	1.621(6)	C(31)–Si(2)	1.876(7)
C(41)–Si(2)	1.864(7)	O(3)–Si(3)	1.619(6)
O(4)–Si(3)	1.612(5)	C(51)–Si(3)	1.871(6)
C(61)–Si(3)	1.865(7)		
O(4)–Ti–O(1)	95.5(2)	N(1)–Ti–O(1)	83.6(2)
N(1)–Ti–O(4)	168.5(1)	O(2)–Si(1)–O(1)	111.2(3)
C(11)–Si(1)–O(1)	111.7(3)	C(11)–Si(1)–O(2)	107.1(3)
C(21)–Si(1)–O(1)	110.6(3)	C(21)–Si(1)–O(2)	106.2(3)
C(21)–Si(1)–C(11)	109.8(3)	O(3)–Si(2)–O(2)	111.2(3)
C(31)–Si(2)–O(2)	109.7(3)	C(31)–Si(2)–O(3)	108.2(3)
C(41)–Si(2)–O(2)	107.4(3)	C(41)–Si(2)–O(3)	110.2(3)
C(41)–Si(2)–C(31)	110.1(3)	O(4)–Si(3)–O(3)	112.2(3)
C(51)–Si(3)–O(3)	108.5(3)	C(51)–Si(3)–O(4)	110.1(3)
C(61)–Si(3)–O(3)	109.5(3)	C(61)–Si(3)–O(4)	109.2(3)
C(61)–Si(3)–C(51)	107.3(3)	Si(1)–O(1)–Ti	151.5(2)
Si(2)–O(2)–Si(1)	146.4(3)	Si(3)–O(3)–Si(2)	156.0(3)
Si(3)–O(4)–Ti	158.2(2)	O(4)–Ti–O(4)	102.6(3)
C(12)–C(11)–Si(1)	120.0(2)	C(16)–C(11)–Si(1)	119.5(2)
C(22)–C(21)–Si(1)	118.7(2)	C(26)–C(21)–Si(1)	121.3(2)
C(32)–C(31)–Si(2)	119.5(2)	C(36)–C(31)–Si(2)	120.4(2)
C(42)–C(41)–Si(2)	118.7(2)	C(46)–C(41)–Si(2)	121.3(2)
C(52)–C(51)–Si(3)	120.1(2)	C(56)–C(51)–Si(3)	119.6(2)
C(62)–C(61)–Si(3)	119.6(2)	C(66)–C(61)–Si(3)	120.3(2)
C(72)–N(1)–Ti	122.1(2)	C(76)–N(1)–Ti	117.9(2)
		N(1)–Ti–N(1′)	79.7(3)

However with dichlorodimethylsilane chain expansion did occur and the cyclic tetrasiloxane $Si_4Me_2Ph_6O_4$ was isolated. These experiments suggested that siloxane chain expansion occurred in order to relieve ring strain energy and not because the precursor disiloxanediolate was intrinscially unstable in the presence of base or metal halide compounds. The formation of the zirconadisiloxane compound (**3**) gave further weight to this suggestion.

Crystallography.—The structures of compounds (**2**) and (**3**) are depicted in Figures 1 and 2. Selected bond lengths and angles are given in Tables 2 and 3 with fractional atomic co-ordinates in Tables 4 and 5. The titanium atom in compound (**2**) has distorted *cis*-octahedral geometry. The eight-membered titanatrisiloxane rings were found to be almost

Table 3. Bonds lengths (Å) and angles (°) for compound (**3**)

Li(2)–Zr	2.716(13)	O(1)–Zr	2.095(5)	C(421)–Si(4)	1.878(8)	O(7)–Si(5)	1.619(7)
O(3)–Zr	2.098(7)	O(4)–Zr	2.131(6)	O(8)–Si(3)	1.642(5)	C(511)–Si(5)	1.875(9)
O(6)–Zr	2.092(7)	O(7)–Zr	2.015(7)	C(521)–Si(5)	1.870(9)	O(8)–Si(6)	1.630(7)
O(9)–Zr	2.101(5)	O(1)–Si(1)	1.622(7)	O(9)–Si(6)	1.621(7)	C(611)–Si(6)	1.884(8)
O(2)–Si(1)	1.615(7)	C(111)–Si(1)	1.879(8)	C(621)–Si(6)	1.867(8)	C(11)–N(1)	1.334(10)
O(1)–Li(1)	2.00(1)	O(6)–Li(1)	2.00(1)	C(15)–N(1)	1.313(13)	C(12)–C(11)	1.372(14)
N(1)–Li(1)	2.09(2)	O(3)–Li(2)	2.07(1)	C(13)–C(12)	1.342(17)	C(14)–C(13)	1.381(13)
O(4)–Li(2)	2.03(1)	N(3)–Li(2)	2.01(2)	C(15)–C(14)	1.376(15)	C(21)–N(2)	1.335(12)
C(121)–Si(1)	1.873(9)	O(2)–Si(2)	1.641(6)	C(25)–N(2)	1.327(14)	C(22)–C(21)	1.392(16)
O(3)–Si(2)	1.616(7)	C(211)–Si(2)	1.870(8)	C(23)–C(22)	1.357(19)	C(24)–C(23)	1.357(17)
C(221)–Si(2)	1.862(9)	O(4)–Si(3)	1.607(7)	C(25)–C(24)	1.391(17)	C(31)–N(3)	1.321(14)
O(5)–Si(3)	1.637(7)	C(311)–Si(3)	1.865(8)	C(35)–N(3)	1.312(18)	C(32)–C(31)	1.391(15)
C(321)–Si(3)	1.872(6)	O(5)–Si(4)	1.640(6)	C(33)–C(32)	1.360(27)	C(34)–C(33)	1.371(26)
O(6)–Si(4)	1.615(7)	C(411)–Si(4)	1.870(8)	C(35)–C(34)	1.446(16)		
O(1)–Zr–Li(2)	125.6(4)	O(3)–Zr–Li(2)	48.8(3)	C(421)–Si(4)–O(6)	110.3(3)	C(421)–Si(4)–C(411)	108.3(8)
O(3)–Zr–O(1)	88.1(3)	O(4)–Zr–Li(2)	47.7(3)	Si(3)–O(4)–Zr	136.1(3)	Si(4)–O(5)–Si(3)	131.1(3)
O(4)–Zr–O(1)	102.8(3)	O(4)–Zr–O(3)	80.8(3)	Si(4)–O(6)–Zr	136.2(2)	C(312)–C(311)–Si(3)	118.6(5)
O(6)–Zr–Li(2)	126.7(4)	O(6)–Zr–O(1)	82.0(3)	C(316)–C(311)–Si(3)	121.3(6)	C(322)–C(321)–Si(3)	118.6(5)
O(6)–Zr–O(3)	160.8(2)	O(6)–Zr–O(4)	85.3(3)	C(326)–C(321)–Si(3)	121.4(5)	C(412)–C(411)–Si(4)	121.4(5)
O(7)–Zr–Li(2)	123.5(4)	O(7)–Zr–O(1)	94.7(3)	C(416)–C(411)–Si(4)	118.6(5)	C(422)–C(421)–Si(4)	118.8(5)
O(7)–Zr–O(3)	104.2(3)	O(7)–Zr–O(4)	162.0(1)	C(426)–C(421)–Si(4)	121.2(4)	O(8)–Si(5)–O(7)	109.0(3)
O(7)–Zr–O(6)	93.0(3)	O(9)–Zr–Li(2)	46.7(3)	C(511)–Si(5)–O(7)	110.4(4)	C(511)–Si(5)–O(8)	109.8(4)
O(9)–Zr–O(1)	168.4(2)	O(9)–Zr–O(3)	80.5(3)	C(521)–Si(5)–O(7)	115.6(4)	C(521)–Si(5)–O(8)	104.4(3)
O(9)–Zr–O(4)	77.8(3)	O(9)–Zr–O(6)	109.6(3)	C(521)–Si(5)–C(511)	107.5(4)	O(9)–Si(6)–O(8)	110.3(3)
O(9)–Zr–O(7)	85.9(3)	O(2)–Si(1)–O(1)	110.6(3)	C(611)–Si(6)–O(8)	105.0(4)	C(611)–Si(6)–O(9)	112.3(4)
C(111)–Si(1)–O(1)	108.1(3)	C(111)–Si(1)–O(2)	109.4(4)	C(621)–Si(6)–O(8)	110.2(4)	C(621)–Si(6)–O(9)	109.0(4)
C(121)–Si(1)–O(1)	114.1(4)	C(121)–Si(1)–O(2)	102.9(4)	C(621)–Si(6)–C(611)	109.9(3)	Si(5)–O(7)–Zr	142.3(2)
C(121)–Si(1)–C(111)	111.6(3)	O(3)–Si(2)–O(2)	109.0(3)	Si(6)–O(8)–Si(5)	133.4(3)	Si(6)–O(9)–Zr	138.6(2)
C(211)–Si(2)–O(2)	107.1(4)	C(211)–Si(2)–O(3)	111.1(3)	C(516)–C(511)–Si(5)	119.6(5)	C(522)–C(521)–Si(5)	119.9(5)
C(221)–Si(2)–O(2)	106.1(3)	C(221)–Si(2)–O(3)	113.4(4)	C(526)–C(521)–Si(5)	119.9(6)	C(612)–C(611)–Si(6)	119.5(4)
C(221)–Si(2)–C(211)	109.7(4)	Si(1)–O(1)–Zr	132.7(3)	C(626)–C(621)–Si(6)	119.6(6)	C(15)–N(1)–C(11)	115.5(8)
Si(2)–O(2)–Si(1)	132.2(3)	Si(2)–O(3)–Zr	138.4(2)	C(12)–C(11)–N(1)	124.4(10)	C(13)–C(12)–C(11)	119.5(8)
C(112)–C(111)–Si(1)	119.8(5)	C(116)–C(111)–Si(1)	120.2(5)	C(14)–C(13)–C(12)	117.3(10)	C(15)–C(14)–C(13)	119.5(11)
C(122)–C(121)–Si(1)	121.5(6)	C(126)–C(121)–Si(1)	118.4(5)	C(14)–C(15)–N(1)	123.7(8)	C(25)–N(2)–C(21)	114.6(9)
C(212)–C(211)–Si(2)	119.9(5)	C(216)–C(211)–Si(2)	120.1(6)	C(22)–C(21)–N(2)	124.6(10)	C(23)–C(22)–C(21)	117.6(11)
C(222)–C(221)–Si(2)	118.9(5)	C(226)–C(221)–Si(2)	121.1(5)	C(24)–C(23)–C(22)	120.6(12)	C(25)–C(24)–C(23)	117.0(12)
O(5)–Si(3)–O(4)	111.1(4)	C(311)–Si(3)–O(4)	110.6(3)	C(24)–C(25)–N(2)	125.5(10)	C(35)–N(3)–C(31)	119.9(9)
C(311)–Si(3)–O(5)	108.9(4)	C(321)–Si(3)–O(4)	113.0(4)	C(32)–C(31)–N(3)	124.0(13)	C(33)–C(32)–C(31)	115.7(13)
C(321)–Si(3)–O(5)	106.3(3)	C(321)–Si(3)–C(311)	106.7(3)	C(34)–C(33)–C(32)	123.4(12)	C(35)–C(34)–C(33)	115.7(16)
O(6)–Si(4)–O(5)	109.4(3)	C(411)–Si(4)–O(5)	109.0(3)	C(34)–C(35)–N(3)	121.1(13)		
C(411)–Si(4)–O(6)	110.4(4)	C(421)–Si(4)–O(5)	109.3(4)				

planar and the Si–O(Si) bond lengths and Si–O–Si angles were close to those previously reported for the tetrahedral compound $[\overline{\mathrm{Ti\{OSiPh_2(OSiPh_2)_3O}}\}_2]$ (**5**). A narrowing of the O–Ti–O angles towards octahedral values [95.5(2) and 102.6(3)°] was accompanied by slight lengthening of the Ti–O bonds [1.874(5)—1.836(5) Å] compared to those in (**5**) [1.777(5)—1.791(5) Å], where some degree of π interaction is likely. The zirconium complex (**3**) showed an octahedral arrangement of the three chelating disiloxanediolate groups, similar to that previously found for the dianion (**4**). A novel feature of the present molecule concerns the internal solvation of the lithium cations with both face- and edge-bridging observed. All six Zr–O distances were slightly different and in the range 2.015(7)—2.131(6) Å, the shortest Zr–O distance being associated with the only oxygen atom not also co-ordinated to lithium. The shortest Zr–O distance in compound (**4**) was 2.070(4) Å. Chelate angles, O–Zr–O, were in the range 85.3(3)—88.1(3)° close to those previously reported. The angles described by the *cis*-O–Zr–O atoms [77.8(3)—109.6(3)°] and the *trans*-O–Zr–O atoms [160.8(2)—168.4(2)°] showed more distortion from regular octahedral values than found in the case of compound (**3**), probably because of the internally solvated lithium atoms.

Experimental

All reactions were carried out in an atmosphere of purified nitrogen. Melting points were recorded on samples sealed in capillaries under nitrogen. Spectrometers: i.r., Perkin-Elmer 577 (spectra in Nujol mulls); n.m.r., Bruker (400 MHz) in $[^2H_8]$toluene at 310 K (data relative to $LiNO_3$ in D_2O or $SiMe_4$ in $[^2H_8]$toluene); mass, Kratos MS 902 (at 70 eV 1.12×10^{-17} J).

cis-$[\overline{\mathrm{Ti\{OSiPh_2(OSiPh_2)_2O}}\}_2(py)_2]\cdot 2C_6H_5Me$ (**2**).—To a solution of $TiCl_4$ (0.276 g, 1.5 mmol) in benzene (40 cm^3) at 0 °C was added a solution of dilithium tetraphenyldisiloxanediolate (**1**) (4.5 mmol) in tetrahydrofuran. The resulting colourless solution was stirred overnight and the thf was then evaporated. The crispy solid residue was stirred in toluene (40 cm^3) and the filtered toluene solution then concentrated to approximately 15 cm^3. Pyridine was added until the solution became turbid and the mixture was then heated until a clear solution was obtained. On slow cooling colourless cubic crystals of compound (**2**) were deposited. Yield 1.26 g (52%), m.p. 97–100 °C. I.r.: 1 600m, 1 590w, 1 430s, 1 115vs, 1 050vs, 1 025s, 920vs, 740m, 715s, 695s, and 525s cm^{-1}.

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for compound (**2**)

Atom	*x*	*y*	*z*
Ti	0	1 292.7(7)	2 500.0
Si(1)	436.5(8)	1 298.1(9)	3 805.6(5)
Si(2)	2 091.2(8)	1 255.9(9)	3 944.2(6)
Si(3)	1 597.1(8)	330.4(9)	2 883.5(6)
O(1)	60(2)	1 447(2)	3 197(1)
O(2)	1 300(2)	1 498(2)	3 980(1)
O(3)	2 019(2)	770(2)	3 420(1)
O(4)	775(2)	632(2)	2 636(1)
C(12)	256(2)	−308(2)	3 609(1)
C(13)	284(2)	−1 081(2)	3 754(1)
C(14)	407(2)	−1 278(2)	4 273(1)
C(15)	502(2)	−702(2)	4 648(1)
C(16)	474(2)	70(2)	4 503(1)
C(11)	352(2)	268(2)	3 983(1)
C(22)	−715(2)	1 936(3)	4 100(2)
C(23)	−1 029(2)	2 402(3)	4 390(2)
C(24)	−593(2)	2 876(3)	4 779(2)
C(25)	157(2)	2 882(3)	4 878(2)
C(26)	471(2)	2 415(3)	4 587(2)
C(21)	35(2)	1 942(3)	4 198(2)
C(32)	3 226(2)	896(3)	4 865(2)
C(33)	3 597(2)	436(3)	5 286(2)
C(34)	3 317(2)	−281(3)	5 357(2)
C(35)	2 665(2)	−537(3)	5 008(2)
C(36)	2 294(2)	−76(3)	4 587(2)
C(31)	2 574(2)	640(3)	4 516(2)
C(42)	2 547(2)	2 760(3)	4 276(2)
C(43)	2 951(2)	3 432(3)	4 304(2)
C(44)	3 417(2)	3 506(3)	4 005(2)
C(45)	3 480(2)	2 907(3)	3 678(2)
C(46)	3 077(2)	2 235(3)	3 651(2)
C(41)	2 610(2)	2 161(3)	3 950(2)
C(52)	2 867(2)	577(2)	2 594(1)
C(53)	3 260(2)	616(2)	2 243(1)
C(54)	2 903(2)	558(2)	1 771(1)
C(55)	2 152(2)	462(2)	1 530(1)
C(56)	1 758(2)	423(2)	1 882(1)
C(51)	2 116(2)	480(2)	2 414(1)
C(62)	1 079(2)	−1 192(3)	2 656(2)
C(63)	1 088(2)	−1 986(3)	2 733(2)
C(64)	1 603(2)	−2 314(3)	3 161(2)
C(65)	2 109(2)	−1 847(3)	3 512(2)
C(66)	2 101(2)	−1 053(3)	3 435(2)
C(61)	1 586(2)	−725(3)	3 007(2)
C(72)	−819(2)	2 865(2)	1 984(1)
C(73)	−1 322(2)	3 463(2)	1 904(1)
C(74)	−1 799(2)	3 499(2)	2 197(1)
C(75)	−1 772(2)	2 937(2)	2 570(1)
C(76)	−1 269(2)	2 339(2)	2 650(1)
N(1)	−792(2)	2 303(2)	2 357(1)
C(1)	4 823(7)	772(11)	3 619(7)
C(2)	5 014(8)	228(12)	3 247(6)
C(3)	4 726(9)	−428(19)	3 332(8)
C(4)	4 371(10)	−724(8)	3 640(8)
C(5)	4 235(8)	−167(12)	3 977(6)
C(6)	4 473(6)	576(10)	3 937(5)
C(7)	5 093(7)	1 469(9)	3 520(7)

$\mathrm{Li_2[\overline{Zr(OSiPh_2OSiPh_2O}})_3]\cdot 3py\cdot 1.5C_6H_5Me$(**3**).—This compound was prepared in the manner described above from $ZrCl_4$ (1.26 g, 5.4 mmol) in thf (40 cm^3) and a solution of (**1**) (1.62 mmol) in thf (40 cm^3). Yield 5.86 g (65%), m.p. 232 °C (Found: C, 67.9; H, 5.0; N, 2.7. Calc. for $C_{97.5}H_{87}Li_2N_3O_9Si_6Zr$: C, 68.2; H, 5.1; N, 2.5%). I.r.: 1 595w, 1 590w, 1 425s, 1 120s, 1 110s, 1 030m, 1 010s, 990s, 940s, 740s, 715m, 700m, and 530s cm^{-1}. N.m.r. at 310 K: ^{29}Si, −40.27(s); ^{7}Li, 1.06(s) p.p.m.

2,2-*Dimethyl*-4,4,6,6,8,8-*hexaphenylcyclotetrasiloxane from* $SiMe_2Cl_2$ *and* $Si_2Ph_4O(OLi)_2$.—To a solution of compound (**1**) (2.4 mmol) in thf (20 cm^3) at 0 °C was added dropwise a solution of $SiMe_2Cl_2$ (0.31 g, 2.4 mmol) in thf (15 cm^3). The reaction mixture was stirred for several hours and then the thf was evaporated. The solid residue was treated with pentane and filtered. A white solid crystallised from the concentrated pentane solution. Yield: 1.62 g, 64% based on $SiMe_2Cl_2$ (Found: C, 68.2; H, 5.5. Calc. for $C_{38}H_{36}O_4Si_4$: C, 68.2; H, 5.5%). ^1H N.m.r. (CD_2Cl_2): 0.1 (s, 6 H, Me_2Si), 7.18—7.3 (m, 12 H), 7.32—7.42 (m, 6 H), and 7.46—7.6 (m, 12 H) *m*/*z* 668(2) $[M]^+$ and 591(100%) $[M - Ph]^+$.

1,1,1,7,7,7-*Hexamethyl*-3,3,5,5-*tetraphenyltetrasiloxane*.—To a solution of compound (**1**) (2.4 mmol) in thf (20 cm^3) at 0 °C was added dropwise $SiMe_3Cl$ (0.52 g, 4.82 mmol) in thf (15 cm^3). The reaction mixture was stirred at room temperature for 6 h and the thf was evaporated. The residue was treated with pentane and the filtered pentane extract dried giving a low-melting white solid. Yield: 1.18 g, 87%. ^1H N.m.r. (CD_2Cl_2): 0.0(s), 7.2—7.43(m), and 7.53—7.64(m). *m*/*z* 558(2) $[M]^+$, 543(28) $[M - Me]^+$, and 481(100%) $[M - Ph]^+$.

Crystallography.—Crystallographic measurements were made on crystals sealed under nitrogen in glass capillaries, using a CAD4 diffractometer operating in the ω—2θ scan mode with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) as previously described.[6] The structures were solved *via* standard heavy-atom procedures and refined using full-matrix least-squares methods,[7] with scattering factors calculated using data from ref. 8. Pyridine rings in compound (**2**) and phenyl groups in (**2**) and (**3**) were treated as rigid hexagons (C–C 1.395 Å, C–C–C 120°), with hydrogen atoms included at a fixed distance (C–H 0.96 Å). Data were corrected for empirical absorption.

Crystal data for compound (**2**). $C_{96}H_{86}N_2O_8Si_6Ti$, M = 1 612.236, monoclinic, a = 19.397(7), b = 17.369(5), c = 27.094(11) Å, β = 108.13(3)°, U = 8 674.96 Å^3, space group $C_{2/c}$, $Z = 4$, D_c = 1.23 g cm^{-3}, μ(Mo-K_α) = 1.98 cm^{-1}, $F(000)$ = 3 368.

Total data recorded 2 724 ($1.5 < \theta < 25.0°$, $\pm h$, $+k$, $+l$), 5 309 unique reflections, 3 432 observed [$I > 1.5\sigma(I)$]. Final R = 0.0595. R' = 0.0699 for 438 parameters, $w = [\sigma^2(F) + 0.000\,605\,F_o^{\,2}]^{-1}$. Final atomic positional parameters are given in Table 4.

Crystal data for compound (**3**). $C_{97.5}H_{87}Li_2N_3O_9Si_6Zr$, M = 1 717.425, triclinic, a = 14.251(3), b = 14.393(4), c = 24.982(5) Å, α = 96.06(2), β = 108.85(2), γ = 114.38(2)°, U = 4 243.84 Å^3, space group = $P\bar{1}$, $Z = 2$, D_c = 1.35 g cm^{-3}, μ = 2.67 g cm^{-1}, $F(000)$ = 1 794.

Total data recorded 9 802 ($1.5 < \theta < 25.0°$, $\pm h$, $+k$, $+l$), 9 637 unique reflections, 6 499 observed [$I > 1.5\sigma(I)$]. Final R = 0.0594, R' = 0.0689 for 1 037 parameters, $w = [\sigma^2(F) +$

Table 5. Fractional atomic co-ordinates (× 10^4) for compound (**3**)

Atom	*x*	*y*	*z*
Zr	4 213.1(5)	1 691.1(4)	2 354.5(3)
Li(1)	3 532(9)	−370(9)	1 569(5)
Li(2)	5 420(9)	2 996(8)	3 347(5)
Si(1)	2 191.6(15)	−499.7(14)	2 519.8(8)
Si(2)	3 116.6(15)	1 279.3(14)	3 489.4(8)
O(1)	3 160(3)	113(3)	2 245(2)
O(2)	2 463(3)	56(3)	3 163(2)
O(3)	3 821(3)	1 951(3)	3 107(2)
C(112)	919(3)	−212(4)	1 591(2)
C(113)	12(3)	−163(4)	1 295(2)
C(114)	−858(3)	−371(4)	1 523(2)
C(115)	−822(3)	−628(4)	2 047(2)
C(116)	85(3)	−676(4)	2 344(2)
C(111)	955(3)	−468(4)	2 116(2)
C(122)	1 262(4)	−2 710(4)	2 139(2)
C(123)	1 100(4)	−3 717(4)	2 192(2)
C(124)	1 643(4)	−3 876(4)	2 672(2)
C(125)	2 347(4)	−3 029(4)	3 099(2)
C(126)	2 509(4)	−2 023(4)	3 047(2)
C(121)	1 967(4)	−1 863(4)	2 566(2)
C(212)	5 001(4)	1 400(4)	4 184(2)
C(213)	5 639(4)	1 404(4)	4 683(2)
C(214)	5 261(4)	1 329(4)	5 160(2)
C(215)	4 245(4)	1 250(4)	5 139(2)
C(216)	3 606(4)	1 246(4)	4 640(2)
C(211)	3 985(4)	1 321(4)	4 163(2)
C(222)	1 183(4)	966(4)	3 749(2)
C(223)	385(4)	1 243(4)	3 836(2)
C(224)	494(4)	2 242(4)	3 802(2)
C(225)	1 402(4)	2 965(4)	3 682(2)
C(226)	2 200(4)	2 688(4)	3 595(2)
C(221)	2 090(4)	1 689(4)	3 629(2)
Si(3)	6 677.1(14)	1 741.7(14)	2 871.1(8)
Si(4)	5 901.3(14)	1 302.5(13)	1 633.9(8)
O(4)	5 607(3)	1 829(3)	2 921(2)
O(5)	6 800(3)	1 714(3)	2 232(2)
O(6)	4 756(3)	1 100(3)	1 742(2)
C(312)	7 532(3)	324(4)	3 062(2)
C(313)	7 516(3)	−606(4)	3 183(2)
C(314)	6 641(3)	−1 319(4)	3 332(2)
C(315)	5 781(3)	−1 102(4)	3 360(2)
C(316)	5 796(3)	−173(4)	3 239(2)
C(311)	6 672(3)	541(4)	3 090(2)
C(322)	8 164(4)	2 917(4)	3 893(2)
C(323)	9 080(4)	3 747(4)	4 238(2)
C(324)	9 749(4)	4 526(4)	4 010(2)
C(325)	9 501(4)	4 476(4)	3 437(2)
C(326)	8 584(4)	3 646(4)	3 092(2)
C(321)	7 916(4)	2 867(4)	3 320(2)
C(412)	5 747(3)	2 894(4)	1 082(2)
C(413)	6 079(3)	3 650(4)	762(2)
C(414)	6 971(3)	3 820(4)	558(2)
C(415)	7 530(3)	3 235(4)	674(2)
C(416)	7 198(3)	2 479(4)	994(2)
C(411)	6 306(3)	2 309(4)	1 198(2)
C(422)	5 294(4)	−299(4)	696(2)
C(423)	5 206(4)	−1 230(4)	411(2)
C(424)	5 661(4)	−1 795(4)	688(2)
C(425)	6 204(4)	−1 429(4)	1 250(2)
C(426)	6 292(4)	−497(4)	1 535(2)
C(421)	5 836(4)	68(4)	1 258(2)
Si(5)	3 004.3(15)	2 948.5(14)	1 602.4(8)
Si(6)	5 063.1(15)	4 360.6(13)	2 446.8(8)
O(7)	3 222(3)	1 999(3)	1 793(2)
O(8)	4 016(3)	4 058(3)	1 939(2)
O(9)	5 127(3)	3 315(3)	2 595(2)
C(512)	1 323(4)	2 331(4)	2 148(2)
C(513)	380(4)	2 282(4)	2 256(2)
C(514)	−142(4)	2 791(4)	1 973(2)
C(515)	280(4)	3 348(4)	1 583(2)
C(516)	1 224(4)	3 397(4)	1 475(2)
C(511)	1 745(4)	2 889(4)	1 757(2)
C(522)	3 633(4)	3 878(4)	703(3)
C(523)	3 507(4)	3 966(4)	146(3)
C(524)	2 652(4)	3 187(4)	−263(3)
C(525)	1 922(4)	2 320(4)	−115(3)
C(526)	2 047(4)	2 233(4)	442(3)
C(521)	2 903(4)	3 012(4)	851(3)
C(612)	3 870(4)	4 930(4)	3 094(2)
C(613)	3 734(4)	5 452(4)	3 555(2)
C(614)	4 623(4)	6 183(4)	3 966(2)
C(615)	5 646(4)	6 392(4)	3 916(2)
C(616)	5 782(4)	5 869(4)	3 456(2)
C(611)	4 893(4)	5 138(4)	3 045(2)
C(622)	6 405(4)	6 085(4)	2 055(3)
C(623)	7 332(4)	6 691(4)	1 906(3)
C(624)	8 153(4)	6 391(4)	1 948(3)
C(625)	8 048(4)	5 485(4)	2 139(3)
C(626)	7 121(4)	4 879(4)	2 287(3)
C(621)	6 299(4)	5 178(4)	2 246(3)
N(1)	2 554(5)	−609(5)	779(3)
C(11)	1 684(7)	−1 505(7)	553(4)
C(12)	1 080(7)	−1 752(7)	15(4)
C(13)	1 357(8)	−1 062(8)	−317(4)
C(14)	2 242(8)	−119(8)	−90(5)
C(15)	2 801(7)	69(7)	455(4)
N(2)	6 393(5)	1 793(5)	8 448(3)
C(21)	6 618(6)	2 530(7)	8 889(4)
C(22)	6 588(7)	3 478(7)	8 860(5)
C(23)	6 275(7)	3 650(7)	8 347(6)
C(24)	6 003(7)	2 916(8)	7 883(5)
C(25)	6 076(6)	2 003(7)	7 961(4)
N(3)	6 322(7)	4 087(5)	4 038(3)
C(31)	7 280(8)	4 758(7)	4 017(4)
C(32)	7 957(10)	5 633(9)	4 431(7)
C(33)	7 584(16)	5 762(11)	4 882(6)
C(34)	6 616(15)	5 077(10)	4 942(6)
C(35)	5 965(11)	4 222(8)	4 473(5)
C(41)	244(12)	4 441(9)	−402(7)
C(42)	833(11)	4 698(12)	131(9)
C(43)	−592(12)	4 760(12)	−545(7)
C(44)	507(19)	3 979(15)	−786(10)
C(52)	9 112(11)	1 915(12)	5 848(10)
C(53)	9 873(11)	2 324(12)	6 360(10)
C(54)	10 854(11)	2 302(12)	6 413(10)
C(55)	11 077(11)	1 872(12)	5 954(10)
C(56)	10 317(11)	1 464(12)	5 442(10)
C(51)	9 334(11)	1 485(12)	5 390(10)
C(57)	8 453(16)	1 102(19)	4 957(11)

0.001 079 $F_o^2]^{-1}$. Final atomic positional parameters are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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