Solid-state and Solution Structures of some Lithium Salts of Tetraphenyldisiloxanediolate(2−) and the Lithium-bridged Compounds $Li_2[\overline{M(OSiPh_2OSiPh_2O})_3{\cdot}3py]$ (py = pyridine, M = Zr or Hf)†

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The compound $[\{Si_2Ph_4O(OLi)_2\}_2{\cdot}3(C_4H_8O_2)]_\infty$ was formed in a 2:1 reaction between *n*-butyllithium and tetraphenyldisiloxanediol in dioxane and its solid-state structure was determined by single-crystal X-ray diffraction. Variable-temperature ^7Li and ambient temperature ^{29}Si NMR studies on $[^2H_8]$toluene solutions of this and the related pyridine (py) adduct $[Si_2Ph_4O(OLi)_2{\cdot}2py]_2$ were carried out. The cyclic hafnasiloxane $Li_2[\overline{Hf(OSiPh_2OSiPh_2O})_3]{\cdot}3py{\cdot}3C_6H_6$ was isolated from a 3:1 reaction between $[Si_2Ph_4O(OLi)_2{\cdot}2thf]_2$ (thf = tetrahydrofuran) and $HfCl_4$ and its structure determined by single-crystal X-ray diffraction. The variable-temperature ^7Li NMR spectra of this and the related zirconium compound show that there is rapid exchange between non-equivalent lithium environments. Lithium hopping between available equivalent environments is inferred by the equilibration of the three distinct silicon environments in the structure as seen by ^{29}Si NMR studies.

A considerable number of reports concerning compounds incorporating metallasiloxane rings have appeared in the recent literature.[1] We have for some time been investigating compounds incorporating six-membered metallasiloxane rings derived from $[Si_2Ph_4O(OLi)_2{\cdot}2thf]_2$ (thf = tetrahydrofuran) and have reported a number of structures wherein such fragments appear. In an earlier paper we reported[2] on the solid-state structure of the pyridine adduct $[Si_2Ph_4O(OLi)_2{\cdot}2py]_2$ **1** (py = pyridine) and we now report on the solid-state structure of the dioxane adduct $[\{Si_2Ph_4O(OLi)_2\}_2{\cdot}3(C_4H_8O_2)]_\infty$ **2** and on the solution behaviour of both compounds.

Cyclic metallasiloxanes of titanium, zirconium and hafnium with six-, eight- and ten-membered metallasiloxane rings have been reported (see Table 1 in ref. 3). Structurally characterised compounds with six-membered metallasiloxane rings are available for zirconium and hafnium. These include the tris(chelated) dianionic compounds $[\overline{M(OSiPh_2OSiPh_2O})_3]^{2-}$ (M = Zr **3** or Hf **4**) obtained in reactions between diphenylsilanediol $Ph_2Si(OH)_2$ and $M(NEt_2)_4$.[4] We have recently reported on the molecular zirconium compound $Li_2[\overline{Zr(OSiPh_2OSiPh_2O})_3]{\cdot}3py$ **5** where one face and one edge of the octahedral core of the structure is bridged by pyridine-solvated lithium.[3] We now report on the hafnium compound $Li_2[\overline{Hf(OSiPh_2OSiPh_2O})_3]{\cdot}3py$ **6** which is isostructural with **5**, and on variable-temperature solution ^7Li NMR studies on both compounds.

Results and Discussion

Synthesis and Solid-state Structures.—The solid-state structure of the pyridine adduct of dilithium tetraphenyldisiloxanediolate, $[Si_2Ph_4O(OLi)_2{\cdot}2py]_2$ **1** consists of a dimeric structure incorporating a folded ladder arrangement of three four-membered lithium-oxygen rings. The solid-state structure of the related dioxane adduct $[\{Si_2Ph_4O(OLi)_2\}_2{\cdot}3(C_4H_8O_2)]_\infty$ **2**, is described here together with variable-temperature ^7Li NMR studies and ambient temperature ^{29}Si NMR studies on both **1** and **2**. Compound **2** was formed in a 2:1 reaction between *n*-butyllithium and tetraphenyldisiloxanediol in 1,4-dioxane. Crystals suitable for X-ray diffraction were obtained on slow cooling of hot dioxane–light petroleum solutions. The structure of **2**, shown in Fig. 1, is similar to **1**, consisting of dimeric, pentacyclic units, comprising two six-membered lithiodisiloxane rings and a folded ladder arrangement of three four-membered lithiooxane rings. However in this case the dimeric units are connected by a dioxane bridge, through the exocyclic bridging lithium ions, forming polymeric chains, as shown in Fig. 2. Crystal data, atomic coordinates, and bond lengths and angles are collected in Tables 1, 2 and 3. The endocyclic lithiums are co-ordinated by dioxane in a terminal, unidentate fashion. As in **1** the *endo–endo* Li(1)–Li(1') distances [2.531(36) Å] are longer than the *endo–exo* Li(1)–Li(2) distances [2.405(33) Å] with the latter much shorter than Li ··· Li distances in metallic lithium (3.04 Å) and gaseous lithium (2.67 Å). There are two distinct co-ordination environments for lithium in the dimeric unit, including two essentially three-co-ordinate exocyclic lithium ions and two essentially four-co-ordinate endocyclic lithium ions (if possible Li ··· Li interactions are ignored). There are also two clearly different silicon environments. The angles at the lithium ions are very similar in both compounds but greatly distorted from regular trigonal or tetrahedral geometry. The average exocyclic framework Li–O distances (1.836, **1**; 1.847 Å, **2**) are shorter than the endocyclic Li–O distances (1.982, **1**; 1.946 Å **2**). Apart from leading to polymer formation, changing the Lewis base from pyridine to dioxane results in significantly more acute $Li_{exo}OSi$ angles *e.g.* Li(2')–O(3)–Si(2) 158.27 (**1**) and 144.86° (**2**). This may suggest that a larger steric effect is exerted by the endocyclic co-ordinated dioxane compared to that of pyridine but is more likely a consequence of the polymeric nature of **2**.

The solvated lithium-bridged tris(chelated) hafnium metallasiloxane **6** was obtained in a manner similar to that described previously for the related zirconium compound. Benzene-solvated crystals of **6** were obtained on slow cooling to room

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

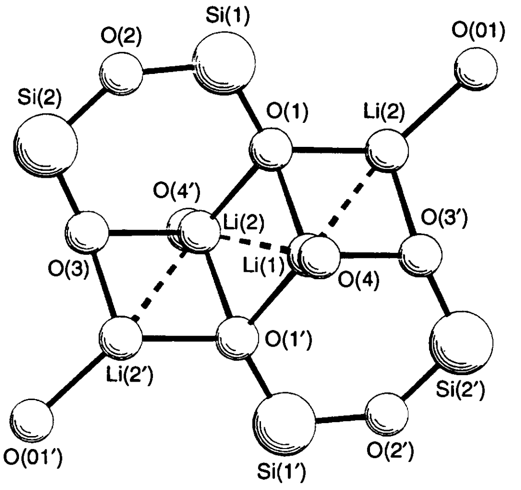


Fig. 1 Dimeric unit of **2** (phenyl groups and dioxane carbon atoms omitted)

Table 1 Crystal data, intensity measurements and structure refinement for compounds **2** and **6***

Formula	$C_{60}H_{64}O_{12}Li_4Si_4$	$C_{87}H_{75}HfLi_2N_3O_9Si_6 \cdot 3C_6H_6$
M	1117.27	1901.793
Space group	$P2_1/n$	$P2_1$
a/Å	16.071(1)	16.521(2)
b/Å	11.504(1)	20.926(1)
c/Å	16.698(1)	13.881(2)
β/°	98.91(1)	92.06(2)
U/Å^3	3049.89 (0.38)	4795.82 (0.93)
D_c/g cm^{-3}	1.217	1.317
F(000)	1176	1956
μ/cm^{-1}	1.49	12.065
Total no. of reflections	4560	9272
No. of unique reflections	3056	8672
No. of observed reflections [$F_o > 3\sigma(F_o)$]	1382	6723
No. of refined parameters	333	1062
Weighting scheme parameter *g* in $w = 1/[\sigma^2(F) + gF^2]$	0.000 23	0.000 032
Final *R*	0.0553	0.0658
Final *R*′	0.0565	0.0572

* Details in common: crystal system, monoclinic; $Z = 2$; Mo-Kα radiation, λ = 0.710 69 Å; θ range $1.5 \leqslant \theta \leqslant 25°$.

Table 2 Fractional atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Si(1)	6 167(2)	938(2)	8 896(2)
Si(2)	6 703(2)	−1 601(2)	9 325(2)
O(1)	5 500(3)	887(4)	9 605(3)
O(2)	6 657(4)	−284(5)	8 932(4)
O(3)	6 063(4)	−1 731(5)	9 948(3)
O(4)	6 425(5)	−138(6)	11 505(4)
O(5)	7 678(7)	38(9)	12 832(6)
O(01)	5 093(4)	3 856(5)	9 764(5)
Li(1)	4 331(11)	379(13)	9 581(9)
Li(2)	5 027(11)	−2 240(15)	10 084(10)
C(1)	6 974(9)	−1 125(11)	11 793(8)
C(2)	7 804(10)	−647(14)	12 129(10)
C(3)	6 288(9)	602(12)	12 151(8)
C(4)	7 150(11)	1 004(13)	12 611(9)
C(01)	4 329(7)	4 530(9)	9 490(9)
C(02)	5 789(7)	4 676(10)	9 854(10)
C(6)	7 285(4)	2 121(5)	10 181(3)
C(7)	7 873(4)	2 963(5)	10 488(3)
C(8)	8 150(4)	3 775(5)	9 967(3)
C(9)	7 838(4)	3 744(5)	9 139(3)
C(10)	7 250(4)	2 901(5)	8 833(3)
C(5)	6 973(4)	2 090(5)	9 354(3)
C(12)	5 765(4)	569(5)	7 272(4)
C(13)	5 440(4)	894(5)	6 480(4)
C(14)	5 024(4)	1 955(5)	6 334(4)
C(15)	4 934(4)	2 691(5)	6 979(4)
C(16)	5 259(4)	2 366(5)	7 770(4)
C(11)	5 675(4)	1 305(5)	7 916(4)
C(19)	8 081(4)	−2 884(5)	10 154(4)
C(20)	8 889(4)	−3 041(5)	10 586(4)
C(21)	9 450(4)	−2 198(5)	10 696(4)
C(22)	9 205(4)	−1 021(5)	10 374(4)
C(23)	8 397(4)	−864(5)	9 942(4)
C(18)	7 836(4)	−1 796(5)	9 832(4)
C(25)	7 120(3)	−3 216(5)	8 115(3)
C(26)	6 925(3)	−4 060(5)	7 515(3)
C(27)	6 090(3)	−4 395(5)	7 274(3)
C(28)	5 450(3)	−3 887(5)	7 631(3)
C(29)	5 645(3)	−3 043(5)	8 231(3)
C(24)	6 480(3)	−2 707(5)	8 472(3)

temperature of hot benzene solutions. The molecular structure is shown in Fig. 3. Crystal data, fractional atomic coordinates and selected bond lengths and angles are given in Tables 1, 4 and 5. The structure of **6** is identical to that previously reported for **5**. The Hf–O distances range from 1.983(10) to 2.181(11) Å and are very similar to related Zr–O distances in **5** as expected. The *cis* O–Hf–O and the *trans* O–Hf–O angles range from 79.2(5) to 109.5(5)° and 162.4(3) to 167.5(3)° respectively. While these ranges are close to those observed in the zirconium compound **5** there is some variation between related angles *e.g.* O(4)–M–O(1) 167.5(3) (M = Hf) and 162.0(1) (M = Zr) and O(7)–M–O(6) 162.4(3) (M = Hf), and 168.4(2)° (M = Zr), so that while distortion from regular octahedral geometry is of a similar magnitude in both compounds it is not identical. The Si–O–Si angles in both **5** and **6** are typical of strained six-membered cyclosiloxanes. The Si–O(Hf) distances are considerably shorter than the Si–O(Si) distances except for Si(6)–O(8) which is unusually long for a Si–O(M) bond. While we are not aware of any precisely analogous structural motifs for tris(chelated) anionic transition metal complexes, face-bridging hydrated potassium is found in a number of tris(oxalato) and dithiooxalato complexes.[5]

We attempted to generate the related dianionic compound analogous to compound **3** with discrete triethylammonium ions from reactions between $Si_2Ph_4O(OH)_2$ and the metal halide $ZrCl_4$ in the presence of triethylamine. Only $(SiPh_2O)_3$ crystallised from diethyl ether extracts of the reaction products. The oligomerisation of $Si_2Ph_4O(OH)_2$ is not apparently promoted by NEt_3 (for example, it may be recovered unchanged from solutions of NEt_3 after 24 h). However, it has generally been our experience in attempts to prepare cyclic compounds bearing the tetraphenyldisiloxanediolate ligand that substantial amounts of $(Ph_2SiO)_3$ are formed when target compounds were either monocyclic {*e.g.* $L_nMOSiPh_2OSiPh_2O$ from $AlMe_3$ (L = Me) or $M[N(SiMe_3)_2]_2$ (L = thf, M = Co, Sr or Ba)}, or anionic spirocyclic with discrete uncomplexed cations {*e.g.* $2NEt_3H^+$ $[M(OSiPh_2OSiPh_2O)_2]^{2-}$ (M = Cr, Co or Cu)} or anionic tris(chelated) octahedral structures. However, when cations may be internally co-ordinated by the tetraphenyldisiloxanediolate ligand, *e.g.* Li^+ or Na^+, then stable complexes and no $(Ph_2SiO)_3$ result, *e.g.* $M'_2[M(OSiPh_2OSiPh_2O)_2]\cdot 4L$ (M = Cr, M′ = Na, L = thf;[6] M = Co, M′ = Li, L = tetramethylethylenediamine;[7] or M = Cu, M′ = Li, L = py[8]). This apparent enhanced stability of alkali metal-bridged compounds compared to related structures with uncomplexed cations may

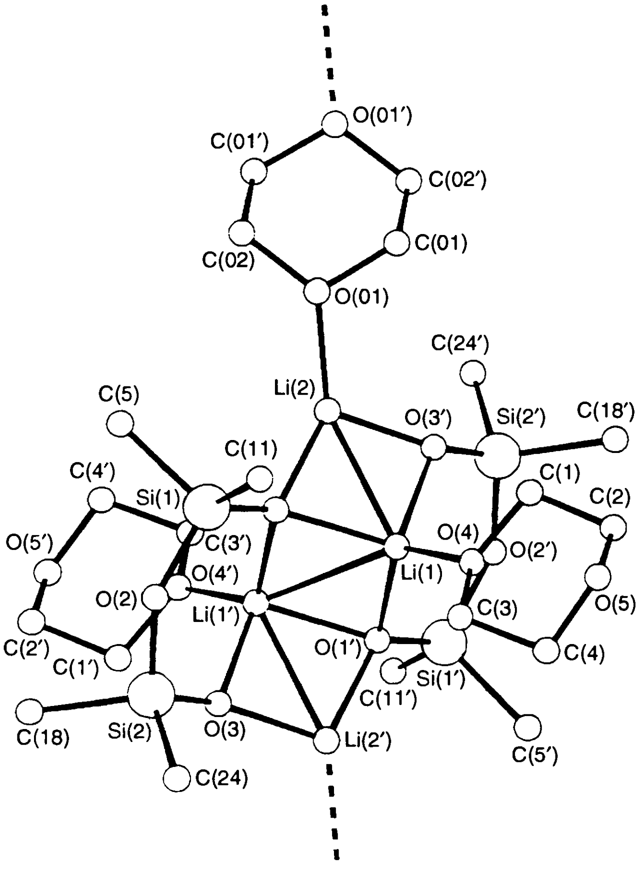


Fig. 2 Chain structure of **2**

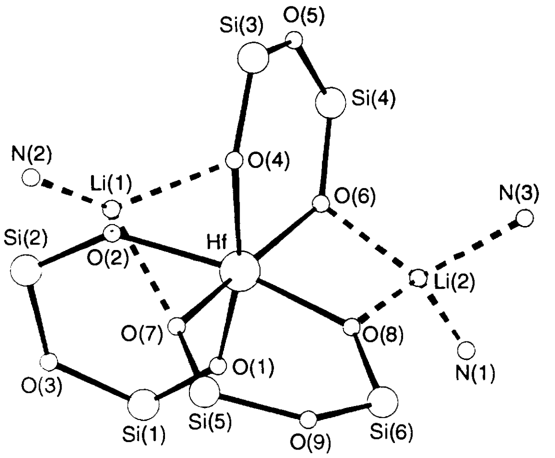


Fig. 3 Molecular structure of **6**

imply the absence of free silanolate ion in solutions of the former. The close association of the alkali metal and silanolate ions may inhibit nucleophilic attack at silicon and thus prevent rearrangement of the ligand. The highly strained monocyclic boron compound $PhB(OSiPh_2OSiPh_2O)$ is the only example of a monocyclic six-membered heteroatomic disiloxane.[9] The predominantly covalent bonding expected around boron in this compound would make dissociation of the silanolate ion unlikely and thus enhance stability compared to related structures having predominantly ionic bonding around the heteroatom.

Table 3 Bond lengths (Å) and angles (°) for compound **2**

O(1)–Si(1)	1.602(8)	O(2)–Si(1)	1.620(8)
O(2)–Si(2)	1.648(8)	O(3)–Si(2)	1.579(8)
C(5)–Si(1)	1.888(8)	C(11)–Si(1)	1.885(9)
C(18)–Si(2)	1.899(9)	C(24)–Si(2)	1.902(8)
Li(1)–O(1)	1.961(19)	Li(2)–O(3')	1.812(21)
Li(1)–O(1')	1.981(17)	Li(1)–O(3')	1.895(18)
Li(2)–O(1)	1.883(18)	Li(1)–O(4)	2.040(22)
Li(2)–O(01)	1.890(20)	Li(1)–Li(2)	2.405(33)
Li(1)–Li(1')	2.531(36)	C(2)–C(1)	1.472(19)
C(4)–C(3)	1.546(21)	C(02)–C(01)	1.461(18)
C(1)–O(4)	1.471(13)	C(3)–O(4)	1.418(13)
C(2)–O(5)	1.454(16)	C(4)–O(5)	1.412(18)
O(2)–Si(1)–O(1)	112.5(4)	O(3)–Si(2)–O(2)	110.8(4)
C(5)–Si(1)–O(1)	108.0(4)	Si(2)–O(2)–Si(1)	140.2(4)
C(5)–Si(1)–O(2)	108.2(4)	C(11)–Si(1)–O(1)	113.3(4)
C(11)–Si(1)–O(2)	106.2(4)	C(11)–Si(1)–C(5)	108.5(4)
C(18)–Si(2)–O(2)	105.5(4)	C(18)–Si(2)–O(3)	111.9(4)
C(24)–Si(2)–O(2)	109.0(4)	C(24)–Si(2)–O(3)	111.3(4)
C(24)–Si(2)–C(18)	108.1(4)	Li(1)–O(1)–Si(1)	137.1(5)
Li(1)–O(3')–Si(2)	119.3(5)	Li(1)–O(1')–Si(1')	115.8(5)
Li(1)–O(3')–Li(2)	80.9(5)	Li(1)–O(1)–Li(2)	77.4(5)
Li(1)–O(1)–Li(1')	79.9(5)	Li(2)–O(3')–Si(2')	144.9(7)
Li(2)–O(1)–Si(1)	121.5(5)	O(1)–Li(1)–O(1')	100.1(5)
O(1)–Li(1)–O(3')	97.3(5)	O(1)–Li(1)–O(4)	119.7(5)
O(4)–Li(1)–O(1')	120.6(5)	O(4)–Li(1)–O(3')	106.8(5)
O(1')–Li(1)–O(3')	109.8(5)	O(01)–Li(2)–O(3')	116.8(5)
O(1)–Li(2)–O(3')	103.2(5)	O(1)–Li(2)–O(01)	135.8(5)
C(3)–O(4)–C(1)	111.7(11)	C(4)–O(5)–C(2)	111.6(13)
C(2)–C(1)–O(4)	107.3(12)	C(1)–C(2)–O(5)	106.2(14)
C(4)–C(3)–O(4)	108.9(13)	C(3)–C(4)–O(5)	110.5(13)
C(6)–C(5)–Si(1)	117.6(3)	C(10)–C(5)–Si(1)	122.4(3)
C(12)–C(11)–Si(1)	121.1(3)	C(16)–C(11)–Si(1)	118.8(3)
C(19)–C(18)–Si(2)	118.2(3)	C(23)–C(18)–Si(2)	121.6(3)
C(25)–C(24)–Si(2)	122.4(3)	C(29)–C(24)–Si(2)	117.6(3)
C(02)–O(01)–C(01)	106.42(4)	C(02)–C(01)–O(01)	107.30(4)
C(01)–C(02)–O(01)	107.22(4)		

Primed atoms related to unprimed equivalents by $1 - x, -y, 2 - z$

NMR Studies.—Compounds **1** *and* **2**. Lithium-7 and ^{29}Si NMR spectra of **1** and **2** were obtained in deuteriated toluene. The ^{7}Li NMR spectrum of compound **2** contains a single resonance at room temperature which broadened slightly on cooling to 183 K. In addition, only one signal was observed in the ^{29}Si NMR spectrum. These observations are inconsistent with the dimeric solid-state structure where there are clearly two different lithium and silicon environments. The molecular weight of compound **1** in solution (determined in consecutive experiments by freezing point depression of benzene) was 730 (for 0.0166 mol dm^{-3} solution) and 750 (for 0.0257 mol dm^{-3} solution), which is, within experimental error, more than half that expected for the solid state structure. This suggests that a monomer–dimer equilibrium occurs in solutions of **1**. A decrease in average molecular weight on dilution was observed as expected, although this was within experimental error. Fig. 4 depicts a possible structure for the monomer. The ^{7}Li NMR spectrum of compound **2** shows a single resonance at room temperature which splits into two broad peaks on cooling to 177 K, with coalescence at 200 K. Two resonances appeared in the ^{29}Si NMR spectrum at room temperature. In addition only one sharp signal was observed for the methylene protons of dioxane. The molecular weight (by freezing point depression of benzene) was only one third of that expected for a dimer unit of the solid-state structure and must represent an average molecular mass of several species in solution. It is clear that the dioxane ligands are labile from the appearance of a single peak for the methylene protons of dioxane in the ^{1}H NMR spectrum. The ^{7}Li NMR studies show that there is exchange of all non-equivalent lithium environments within the solution species at room temperature. Further speculation regarding the nature of species in solutions of **2** is not appropriate at this point.

Compounds **5** *and* **6**.—The molecular weight of **6** as determined by freezing point depression of benzene solutions was 1560 which is close to the relative molecular mass. The presence

Table 4 Fractional atomic coordinates (× 10^4) for compound **6**

Atom	*x*	*y*	*z*
Hf	7 763(1)	−16(1)	1 185(1)
Si(1)	8 761(3)	−396(2)	3 274(3)
Si(2)	6 978(2)	−180(2)	3 442(3)
Si(3)	6 006(3)	−281(2)	−151(3)
Si(4)	7 198(3)	−1 360(2)	22(3)
Si(5)	7 981(3)	1 659(2)	1 276(3)
Si(6)	9 091(3)	960(2)	−56(3)
O(1)	8 633(5)	−235(4)	2 150(5)
O(2)	6 942(4)	−108(5)	2 287(5)
O(3)	7 918(5)	−229(4)	3 830(5)
O(4)	6 664(5)	167(4)	399(5)
O(5)	6 328(6)	−1 023(5)	−195(7)
O(6)	7 823(6)	−841(4)	460(6)
O(7)	7 569(6)	986(4)	1 541(6)
O(8)	8 574(6)	317(4)	207(6)
O(9)	8 692(6)	1 587(5)	464(7)
C(2)	10 247(5)	−201(4)	4 351(5)
C(3)	10 876(5)	167(4)	4 754(5)
C(4)	10 866(5)	830(4)	4 644(5)
C(5)	10 228(5)	1 124(4)	4 131(5)
C(6)	9 599(5)	755(4)	3 728(5)
C(1)	9 608(5)	93(4)	3 838(5)
C(8)	9 624(5)	−1 552(4)	2 972(5)
C(9)	9 812(5)	−2 194(4)	3 139(5)
C(10)	9 390(5)	−2 542(4)	3 816(5)
C(11)	8 781(5)	−2 248(4)	4 326(6)
C(12)	8 592(5)	−1 607(4)	4 160(5)
C(7)	9 014(5)	−1 259(4)	3 483(5)
C(14)	6 234(5)	−915(4)	4 830(6)
C(15)	5 889(5)	−1 462(4)	5 217(6)
C(16)	5 728(5)	−1 992(4)	4 632(6)
C(17)	5 912(5)	−1 975(4)	3 659(6)
C(18)	6 257(5)	−1 428(4)	3 272(6)
C(13)	6 418(5)	−898(4)	3 857(6)
C(20)	7 066(5)	951(4)	4 600(5)
C(21)	6 745(5)	1 477(4)	5 070(5)
C(22)	5 917(5)	1 607(4)	4 981(5)
C(23)	5 410(5)	1 209(4)	4 423(5)
C(24)	5 731(5)	683(4)	3 953(5)
C(19)	6 559(5)	553(4)	4 042(5)
Li(1)	6 377(15)	712(13)	1 604(16)
Li(2)	8 765(13)	−539(13)	−350(15)
N(1)	9 822(8)	−1 005(7)	−9(10)
C(011)	9 808(12)	−1 556(10)	394(12)
C(012)	10 454(14)	−1 975(10)	549(12)
C(013)	11 157(14)	−1 746(11)	281(13)
C(014)	11 202(12)	−1 178(11)	−108(13)
C(015)	10 513(13)	−824(11)	−202(14)
N(2)	5 494(8)	1 358(6)	1 784(9)
C(021)	4 757(12)	1 323(10)	1 457(12)
C(022)	4 190(12)	1 794(12)	1 530(15)
C(023)	4 409(13)	2 337(10)	2 041(13)
C(024)	5 148(15)	2 347(12)	2 413(16)
C(025)	5 674(12)	1 882(10)	2 250(12)
N(3)	8 617(8)	−471(6)	−1 793(8)
C(031)	8 005(8)	−137(6)	−2 103(10)
C(032)	7 827(9)	−76(9)	−3 100(10)
C(033)	8 332(13)	−343(9)	−3 731(11)
C(034)	8 949(14)	−664(11)	−3 402(11)
C(035)	9 117(10)	−733(8)	−2 431(11)
C(26)	4 283(5)	−147(3)	58(5)
C(27)	3 573(5)	−173(3)	571(5)
C(28)	3 603(5)	−359(3)	1 537(5)
C(29)	4 343(5)	−519(3)	1 990(5)
C(30)	5 053(5)	−492(3)	1 477(5)
C(25)	5 023(5)	−307(3)	511(5)
C(32)	5 391(5)	−429(5)	−2 054(5)
C(33)	5 146(5)	−218(5)	−2 972(5)
C(34)	5 291(5)	412(5)	−3 245(5)
C(35)	5 681(5)	831(5)	−2 599(5)
C(36)	5 927(5)	620(5)	−1 681(5)
C(31)	5 782(5)	−10(5)	−1 409(5)
C(38)	7 629(6)	−2 189(4)	1 558(6)
C(39)	7 542(6)	−2 739(4)	2 111(6)
C(40)	6 865(6)	−3 130(4)	1 961(6)
C(41)	6 275(6)	−2 969(4)	1 259(6)
C(42)	6 362(6)	−2 418(4)	706(6)
C(37)	7 039(6)	−2 028(4)	856(6)
C(44)	7 248(5)	−1 548(4)	−2 030(5)
C(45)	7 537(5)	−1 836(4)	−2 856(5)
C(46)	8 118(5)	−2 318(4)	−2 774(5)
C(47)	8 409(5)	−2 514(4)	−1 865(5)
C(48)	8 119(5)	−2 227(4)	−1 038(5)
C(43)	7 539(5)	−1 744(4)	−1 121(5)
C(50)	8 079(5)	2 088(4)	3 212(5)
C(51)	8 439(5)	2 404(4)	4 002(5)
C(52)	9 182(5)	2 712(4)	3 912(5)
C(53)	9 565(5)	2 703(4)	3 033(5)
C(54)	9 205(5)	2 387(4)	2 243(5)
C(49)	8 463(5)	2 079(4)	2 332(5)
C(56)	6 668(5)	1 932(4)	−14(6)
C(57)	6 075(5)	2 312(4)	−470(6)
C(58)	5 987(5)	2 949(4)	−198(6)
C(59)	6 491(5)	3 206(4)	531(6)
C(60)	7 083(5)	2 826(4)	988(6)
C(55)	7 171(5)	2 189(4)	716(6)
C(62)	8 425(5)	1 571(4)	−1 751(5)
C(63)	8 355(5)	1 689(4)	−2 740(5)
C(64)	8 897(5)	1 408(4)	−3 360(5)
C(65)	9 510(5)	1 009(4)	−2 992(5)
C(66)	9 580(5)	891(4)	2 004(5)
C(61)	9 038(5)	1 172(4)	−1 383(5)
C(68)	10 780(5)	1 192(4)	−127(5)
C(69)	11 575(5)	1 147(4)	240(5)
C(70)	11 743(5)	810(4)	1 092(5)
C(71)	11 117(5)	518(4)	1 575(5)
C(72)	10 321(5)	563(4)	1 207(5)
C(67)	10 153(5)	900(4)	356(5)
C(041)	3 230(5)	876(5)	5 603(6)
C(042)	3 260(5)	351(5)	4 986(6)
C(043)	3 199(5)	440(5)	3 990(6)
C(044)	3 109(5)	1 054(5)	3 611(6)
C(045)	3 079(5)	1 579(5)	4 227(6)
C(046)	3 140(5)	1 490(5)	5 223(6)
C(051)	3 495(6)	8 132(4)	3 197(7)
C(052)	3 462(6)	8 311(4)	4 163(7)
C(053)	2 755(6)	8 578(4)	4 508(7)
C(054)	2 081(6)	8 666(4)	3 888(7)
C(055)	2 114(6)	8 487(4)	2 922(7)
C(056)	2 821(6)	8 220(4)	2 577(7)
C(061)	2 690(5)	10 067(3)	7 991(4)
C(062)	1 886(5)	10 244(3)	7 798(4)
C(063)	1 364(5)	9 831(3)	7 290(4)
C(064)	1 646(5)	9 241(3)	6 974(4)
C(065)	2 449(5)	9 064(3)	7 167(4)
C(066)	2 971(5)	9 478(3)	7 676(4)

of non-co-ordinated toluene in the lattice of the zirconium compound $Li_2[\overline{Zr(OSiPh_2OSiPh_2O})_3]\cdot 3py\cdot 1.5C_6H_5Me$, **5**·$1.5C_6H_5Me$, resulted in observation of an average value, 887, for the molecular weight.

There are clearly two different co-ordination environments for lithium in the zirconium and hafnium compounds **5** and **6**. In addition there are three distinct silicon environments in the molecules. These include (see structure **I** in Scheme 1) three silicons a, bonded to oxo anions of the face bridged by lithium, two silicons b, bonded to oxo anions of the edge bridged by lithium, and one silicon c bonded to the only two-co-ordinate oxo anions in the solid-state structure. However, despite the presence of three distinct silicon environments and two distinct lithium environments, the room-temperature ^{29}Si and ^{7}Li NMR

Table 5 Selected bond lengths (Å) and angles (°) for compound **6**

O(1)–Hf	1.983(10)	O(2)–Hf	2.090(9)	C(37)–Si(4)	1.839(11)	C(43)–Si(4)	1.881(11)
O(4)–Hf	2.120(10)	O(6)–Hf	2.003(11)	O(7)–Si(5)	1.612(12)	O(9)–Si(5)	1.663(12)
O(7)–Hf	2.181(11)	O(8)–Hf	2.062(11)	C(49)–Si(5)	1.864(11)	C(55)–Si(5)	1.885(11)
Li(1)–Hf	2.829(28)	Li(2)–Hf	2.954(26)	O(8)–Si(6)	1.642(12)	O(9)–Si(6)	1.646(13)
O(1)–Si(1)	1.603(10)	O(3)–Si(1)	1.653(11)	C(61)–Si(6)	1.894(10)	C(67)–Si(6)	1.830(11)
C(1)–Si(1)	1.881(11)	C(7)–Si(1)	1.875(11)	Li(1)–O(2)	2.157(29)	Li(1)–O(4)	2.093(27)
O(2)–Si(2)	1.609(10)	O(3)–Si(2)	1.627(11)	Li(2)–O(6)	2.052(26)	Li(1)–O(7)	2.056(28)
C(13)–Si(2)	1.866(11)	C(19)–Si(2)	1.890(11)	Li(2)–O(8)	1.981(30)	N(2)–Li(1)	2.011(31)
O(4)–Si(3)	1.608(11)	O(5)–Si(3)	1.643(13)	N(1)–Li(2)	2.041(28)	N(3)–Li(2)	2.014(26)
C(25)–Si(3)	1.895(11)	C(31)–Si(3)	1.860(10)	C(011)–N(1)	1.282(25)	C(015)–N(1)	1.240(26)
O(5)–Si(4)	1.620(13)	O(6)–Si(4)	1.602(12)				
O(2)–Hf–O(1)	87.6(4)	O(4)–Hf–O(1)	167.5(3)	C(49)–Si(5)–O(9)	106.5(6)	C(55)–Si(5)–O(7)	108.0(6)
O(4)–Hf–O(2)	80.0(4)	O(6)–Hf–O(1)	95.3(4)	C(55)–Si(5)–O(9)	106.4(6)	C(55)–Si(5)–C(49)	108.9(5)
O(6)–Hf–O(2)	109.5(5)	O(6)–Hf–O(4)	87.4(4)	O(9)–Si(6)–O(8)	109.6(6)	C(61)–Si(6)–O(8)	113.7(5)
O(7)–Hf–O(1)	100.3(4)	O(7)–Hf–O(2)	79.5(5)	C(61)–Si(6)–O(9)	103.5(6)	C(67)–Si(6)–O(8)	112.0(6)
O(7)–Hf–O(4)	79.2(4)	O(7)–Hf–O(6)	162.4(3)	C(67)–Si(6)–O(9)	108.2(6)	C(67)–Si(6)–C(61)	109.3(5)
O(8)–Hf–O(1)	92.9(4)	O(8)–Hf–O(2)	165.2(4)	Si(1)–O(1)–Hf	140.6(5)	Si(2)–O(2)–Hf	137.4(4)
O(8)–Hf–O(4)	99.5(4)	O(8)–Hf–O(6)	85.2(4)	Li(1)–O(2)–Hf	83.5(8)	Li(1)–O(2)–Si(2)	120.9(9)
O(8)–Hf–O(7)	85.9(4)	Li(1)–Hf–O(1)	123.9(6)	Si(2)–O(3)–Si(1)	131.9(5)	Si(3)–O(4)–Hf	133.8(5)
Li(1)–Hf–O(2)	49.3(6)	Li(1)–Hf–O(4)	47.4(5)	Li(1)–O(4)–Hf	84.4(8)	Li(1)–O(4)–Si(3)	121.9(9)
Li(1)–Hf–O(6)	128.5(7)	Li(1)–Hf–O(7)	46.3(6)	Si(4)–O(5)–Si(3)	133.7(7)	Si(4)–O(6)–Hf	137.1(6)
Li(1)–Hf–O(8)	120.2(7)	Li(2)–Hf–O(1)	89.4(6)	Li(2)–O(6)–Hf	93.5(9)	Li(2)–O(6)–Si(4)	119.5(9)
Li(2)–Hf–O(2)	152.8(6)	Li(2)–Hf–O(4)	100.8(6)	Si(5)–O(7)–Hf	136.2(5)	Li(1)–O(7)–Hf	83.7(9)
Li(2)–Hf–O(6)	43.9(6)	Li(2)–Hf–O(7)	127.6(7)	Li(1)–O(7)–Si(5)	131.8(9)	Si(6)–O(8)–Hf	141.1(5)
Li(2)–Hf–O(8)	42.0(6)	Li(2)–Hf–Li(1)	145.7(6)	Li(2)–O(8)–Hf	93.9(8)	Li(2)–O(8)–Si(6)	124.3(9)
O(3)–Si(1)–O(1)	109.1(6)	C(1)–Si(1)–O(1)	111.1(5)	Si(6)–O(9)–Si(5)	132.3(6)	C(1)–C(2)–C(3)	120.0(9)
C(1)–Si(1)–O(3)	108.6(5)	C(7)–Si(1)–O(1)	111.9(5)	O(2)–Li(1)–Hf	47.2(5)	O(4)–Li(1)–Hf	48.2(6)
C(7)–Si(1)–O(3)	108.5(5)	C(7)–Si(1)–C(1)	107.5(5)	O(4)–Li(1)–O(2)	79.1(10)	O(7)–Li(1)–Hf	50.0(7)
O(3)–Si(2)–O(2)	109.7(5)	C(13)–Si(2)–O(2)	112.5(6)	O(7)–Li(1)–O(2)	80.8(10)	O(7)–Li(1)–O(4)	82.7(10)
C(13)–Si(2)–O(3)	109.0(5)	C(19)–Si(2)–O(2)	111.2(6)	N(2)–Li(1)–Hf	169.8(13)	N(2)–Li(1)–O(2)	141.6(13)
C(19)–Si(2)–O(3)	105.4(5)	C(19)–Si(2)–C(13)	108.9(5)	N(2)–Li(1)–O(4)	130.7(12)	N(2)–Li(1)–O(7)	121.2(15)
O(5)–Si(3)–O(4)	110.7(6)	C(25)–Si(3)–O(4)	111.3(5)	O(6)–Li(2)–Hf	42.6(5)	O(8)–Li(2)–Hf	44.1(5)
C(25)–Si(3)–O(5)	106.0(6)	C(31)–Si(3)–O(4)	112.1(5)	O(8)–Li(2)–O(6)	86.0(10)	N(1)–Li(2)–Hf	120.5(11)
C(31)–Si(3)–O(5)	107.9(6)	C(31)–Si(3)–C(25)	108.6(5)	N(1)–Li(2)–O(6)	112.7(13)	N(1)–Li(2)–O(8)	119.3(13)
O(6)–Si(4)–O(5)	109.3(6)	C(37)–Si(4)–O(5)	107.6(6)	N(3)–Li(2)–Hf	129.8(12)	N(3)–Li(2)–O(6)	119.9(12)
C(37)–Si(4)–O(6)	112.4(6)	C(43)–Si(4)–O(5)	108.6(6)	N(3)–Li(2)–O(8)	108.0(14)	N(3)–Li(2)–N(1)	109.7(13)
C(43)–Si(4)–O(6)	113.6(6)	C(43)–Si(4)–C(37)	105.1(5)	C(011)–N(1)–Li(2)	120.1(15)	C(015)–N(1)–Li(2)	126.1(16)
O(9)–Si(5)–O(7)	112.9(6)	C(49)–Si(5)–O(7)	113.9(5)	C(015)–N(1)–C(011)	113.6(18)		

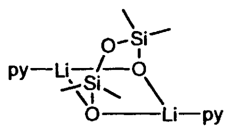
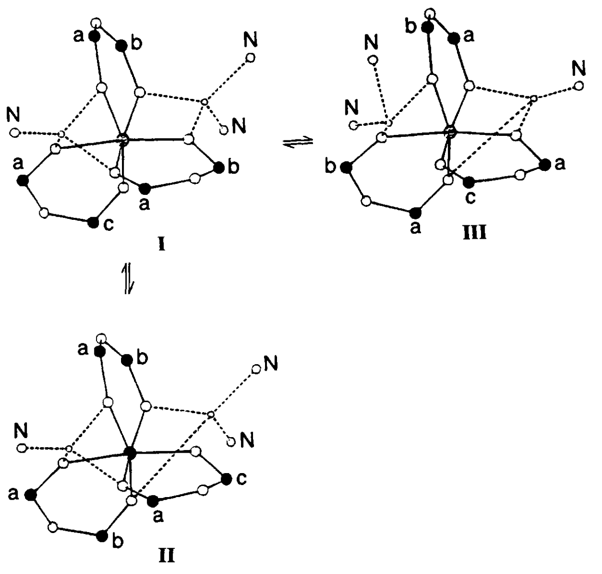


Fig. 4 Possible structure of a monomer of **1**



Scheme 1 Possible silicon environments in compounds **5** and **6**; ○ = Oxygen, ● = silicon, ○ = lithium, ● = zirconium or hafnium

spectra of compounds **5** and **6** show only a single resonance in each case. This suggests that an exchange process is in operation. The manner in which the silicon sites might exchange was partly revealed when variable-temperature ^{7}Li NMR studies were carried out. The single resonance observed in the ^{7}Li NMR spectra at ambient temperature splits in two on cooling to 183 K, see Fig. 5. This implies rapid exchange of the edge- and face-bridging lithiums at room temperature with the solid-state structure freezing out at low temperature. Exchange might be accomplished as shown in Fig. 5 by transfer of pyridine from the edge-bridging lithium site (which subsequently adopts face-bridging co-ordination) to the face-bridging lithium site (which subsequently adopts edge-bridging co-ordination). The observed molecular weight of **6** in solution suggests an associative exchange mechanism as free pyridine would lead to an average molecular weight of half the expected value.

The exchange of face- and edge-bridging lithiums is accompanied by exchange of silicon sites a and b, and a and c (see **I** $\rightleftharpoons$ **III**, Scheme 1) but does not effect exchange of sites b and c. Exchange of sites b and c is accomplished if the edge-bridging lithium is allowed to hop between alternative available edges. There are three identical edges available to lithium and hopping between two of these is illustrated in Scheme 1 (an intermediate species with two face-bridging lithiums is implied). We are not aware of any other reported indications of analogous intramolecular co-ordinated cation mobility in molecular structures. The variable-temperature behaviour (as shown by ^{7}Li NMR studies) of the zirconium compound **5** was similar to that of **6**.

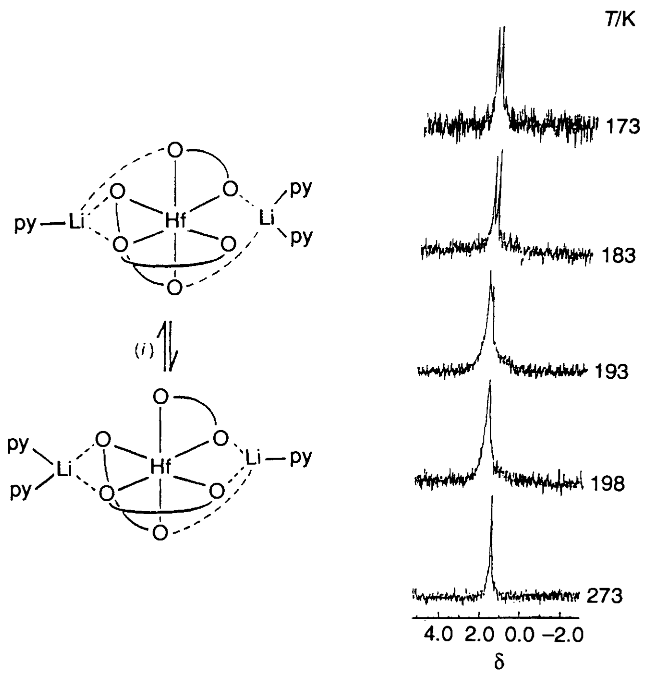


Fig. 5 Variable-temperature ^{7}Li NMR spectra for compound **6**: (*i*) $\Delta G^\ddagger = 38.96 \pm 0.11$ kJ mol^{-1} (calculated using the Eyring equation)

Variable-temperature ^{7}Li NMR studies on solutions of compound **6** with added pyridine was also investigated and the spectra are shown in Fig. 6. The single resonance observed at ambient temperature splits into two below 205 K and the higher-field member of the pair splits into two again below 195 K. The observed splitting may be interpreted in terms of the equilibria also shown in Fig. 6. The lower temperature coalescence is attributed to the exchange of face- and edge-bridged lithiums which in the presence of excess pyridine might occur by initial co-ordination of pyridine at the face-bridging lithium which subsequently adopts edge co-ordination at one of the three available edges. Face bridging may then be regenerated by dissociation of pyridine from either of the edge-bridged lithium sites. The higher temperature coalescence results in the appearance of a signal which is downfield of the rest indicating a more deshielded environment. We attribute this to the formation of discrete pyridine-solvated lithium ions.

Experimental

All manipulations were carried out in an atmosphere of purified nitrogen. Lithium-7 and ^{29}Si NMR data were acquired with a Bruker (400 MHz) spectrometer in [^{2}H$_8$]toluene (chemical shifts, δ, in ppm, relative to LiCl in D_2O or $SiMe_4$ in [^{2}H$_8$]toluene).

Preparations.—Compound **1** was prepared as previously described.[2] ^{29}Si NMR (in 10% [^{2}H$_8$]toluene) δ −44.343 (s).

$[\{Si_2Ph_4O(OLi)\}_2{\cdot}3(C_4H_8O_2)]_\infty$ **2**. A solution of *n*-butyllithium (3.9 cm^3 of 2.7 mol dm^{-3} solution in hexanes, 10.46 mmol) was added dropwise to a stirred solution of tetraphenyldisiloxanediol (2.17 g, 5.23 mmol) in dioxane (60 cm^3) at room temperature. After stirring overnight the colourless solution obtained was concentrated to 20 cm^3 and light petroleum (b.p. 40–60 °C, 20 cm^3) added. A white polycrystalline mass rapidly separated and was filtered off (2.6 g, 45%). Colourless single crystals with cubic faces were subsequently deposited from the filtrate, m.p. 170 °C (decomp.). NMR: ^{1}H ([^{2}H$_8$]toluene), δ 3.28 (s, $C_4H_8O_2$), 7.20 (m, C_6H_5); ^{7}Li (10% [^{2}H$_8$]toluene), δ 1.29 (s) (297 K); 1.78 (br s), 0.73 (br s) (177 K). ^{29}Si (10% [^{2}H$_8$]toluene), δ −39.639 (s), −41.137 (s).

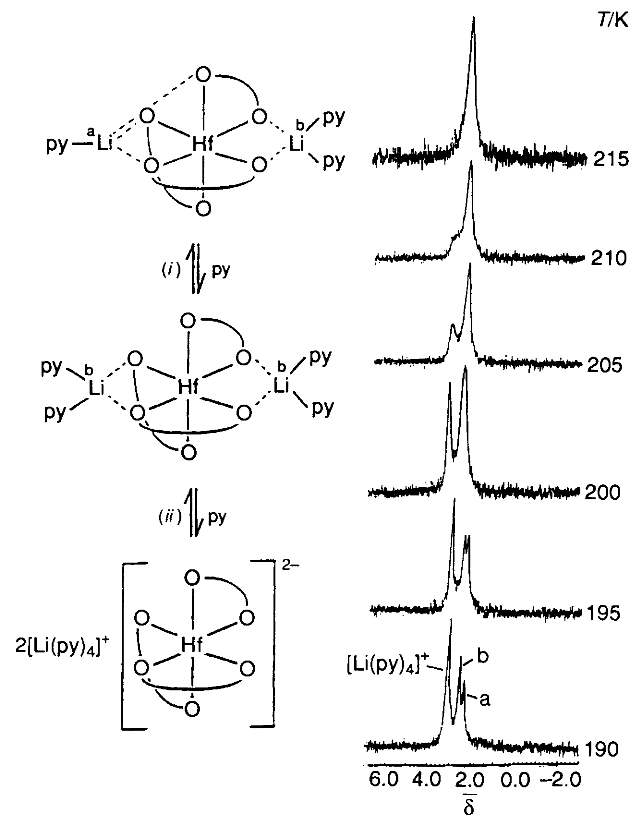


Fig. 6 Variable-temperature ^{7}Li NMR spectra for compound **6** with added pyridine: (*i*) $\Delta G^\dagger = 39.35 \pm 0.11$ kJ mol^{-1}; (*ii*) $\Delta G^\ddagger = 40.37 \pm 0.10$ kJ mol^{-1} (calculated using the Eyring equation)

Compound **5** was prepared as previously described.[3] ^{7}Li NMR: δ 1.95 (s) (285 K); δ 2.85 (s), 2.42 (s) (180 K); T_c 188 K; $\Delta G^\ddagger$ 37.87 kJ mol^{-1}.

$Li_2[Hf(OSiPh_2OSiPh_2O)_3]{\cdot}3py{\cdot}3C_6H_6$ **6**·$3C_6H_6$. An ice-cooled solution of $HfCl_4$ (0.64 g, 2.01 mmol) in thf (20 cm^3), was treated dropwise with a solution containing $Si_2Ph_4O(OLi)_2$ (6.03 mmol) in a mixture of thf and hexane. The reaction mixture was stirred overnight. The solvent was evaporated and the residue extracted with toluene and filtered. The filtered toluene extract was concentrated to 20 cm^3 and pyridine was added until the colourless solution became turbid. A white precipitate was deposited and was redissolved in hot benzene; upon slow cooling colourless cubic crystals formed. Yield 3.12 g, 71.7%, m.p. 132 °C (loses solvent), 294 °C complete melting. IR: 1597w, 1461w, 1428s, 1114s, 1034m, 1016s, 991m, 940s, 907m, 741m, 717s, 698s, 529s cm^{-1}. NMR: ^{29}Si, δ −38.54 (s); ^{7}Li, δ 1.15 (s) (297 K); δ 1.85 (s), 2.08 (s) (183 K), T_c 195.5 K; ^{7}Li (added pyridine), δ 2.43 (s) (215 K), δ 2.46 (s, Li^a and Li^b), 3.14 {s, $[Li(py)_4]^+$} (200 K), T_c [equilibrium (ii)] 208 K; δ 2.39 (s, Li^a), 2.63 (s, Li^b), 3.18 {s, $[Li(py)_4]^+$ (190 K), T_c equilibrium (i)] 198 K.

X-Ray Crystallography.—Data were recorded with a CAD4 diffractometer operating in the ω–2θ scan mode. The structures were solved by standard heavy-atom techniques and refined by least squares,[10] with phenyl groups treated as rigid hexagons [(C–C 1.395 Å, C–C–C 120°), and with inclusion of hydrogen atoms at fixed positions (C–H 0.96 Å)]. The thermal parameters of all the dioxane carbon atoms were high and of the eight hydrogens present in each dioxane ring only one attached to each of C(01), C(2), C(3) and C(4) appeared in the difference map. These refined satisfactorily in terms of isotropic thermal parameters. Crystal data for **2** and **6** are collected in Table 1. Atomic coordinates and bond lengths and angles for **2** are in Tables 2 and 3. The pyridine rings showed some thermal disorder so refinement was initiated with fixed positional and thermal parameters but the rings were allowed to refine freely after the first cycle. For compound **6**, bond lengths and angles and positional parameters are in Tables 4 and 5, respectively.

Acknowledgements

We thank the SERC for a Research Studentship to D. S. and Mr. Harold Toms and Mr. Peter Haycock of the University of London Intercollegiate Research Services NMR Service for obtaining ^{7}Li and ^{29}Si NMR spectra.

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Received 10*th February* 1993; *Paper* 3/00818E