Chemistry of 2,3-Dihydro-2-metallaphenalenes. Part 1. Synthesis of $CHRSiMe_2CHR'C_{10}H_6$ (R = R′ = H; R = R′ = $SiMe_3$; and R,R′ = H,$SiMe_3$) and Formation of the Compound $[\{Li(Me_2NCH_2CH_2NMe_2)\}_2\{CHSiMe_2C(SiMe_3)C_{10}H_6\}]$ † *via* Decomposition of $[\{Li(Me_2NCH_2CH_2NMe_2)\}_2\{1,8\text{-}(CHSiMe_3)_2C_{10}H_6\}]$; Crystal Structures of two Polymorphs of the Silicon Heterocycle Dilithium Complex

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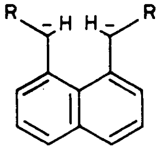
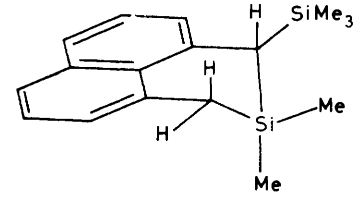
The complexes $[\{Li(tmen)\}_2\{1,8\text{-}(CHSiMe_3)_2C_{10}H_6\}]$ (9) (tmen = *NNN′N′*-tetramethylethylenediamine) and $[\{Li(tmen)\}\{CHSiMe_2CH_2C_{10}H_6\}]$ (13) have been prepared *via* metallation of species formed by *in situ* Grignard trapping reactions of $1,8\text{-}(ClCH_2)_2C_{10}H_6$ with $SiMe_3Cl$ and $SiMe_2Cl_2$ respectively; synthesis of the siline, *meso*-$CH(SiMe_3)SiMe_2CH(SiMe_3)C_{10}H_6$ from (9) is also described. In hexane, (9) decomposes to $[\{Li(tmen)\}_2\{CHSiMe_2C(SiMe_3)C_{10}H_6\}]$ (10) to yield the compound $CH_2SiMe_2CH(SiMe_3)C_{10}H_6$ on the addition of aqueous HCl, the same product as that obtained from a reaction of (13) with $SiMe_3Cl$. The nature of (10) has been established by *X*-ray structure determination of two polymorphs, α and β, which differ both in the mode of interaction of the $Li(tmen)^+$ moieties with the carbanion [$\eta^6:\eta^3$ (α), *cf.* $\eta^4:\eta^3$ (β)] and the conformation of the heterocyclic ring.

In *peri*-naphthalenes steric compression imposed by the close proximity of the substituents can have a dramatic effect on their structure and reactivity, particularly so for bulky groups such as $^-Bu^t$,[1] $^-SnMe_3$,[2] $^-GeMe_3$,[2] and $^-PMe_2$[3] which are necessarily disposed on opposite sides of the aromatic plane. The effect on reactivity is highlighted by the reaction of 1,8-dilithionaphthalene with $SiMe_3Cl$ to yield $1\text{-}(Me_3SiCH_2\text{-}SiMe_2)C_{10}H_7$ rather than the predicted product, $1,8\text{-}(Me_3Si)_2\text{-}C_{10}H_6$.[4] N.m.r. temperature dependence characteristics of *peri*-naphthalene are also unusual for both bulky substituted compounds, exemplified by a large barrier to interconversion flipping of the $1,8\text{-}Bu^t_2$ groups,[5] and in heterocyclic derivatives, *e.g.* 2,3-dihydro-2-metallaphenalenes, for a ring inversion process.[6-8]

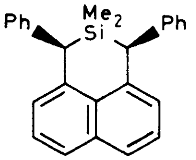
This paper deals with novel *peri*-naphthalenes substituted at the *peri*-carbon atoms by silyl groups and includes silines of the type possessing $SiMe_2$ bridging the *peri*-positions. In subsequent papers this theme will be further developed and will include transition metal metallepines, often designated as metallacycles, based on compounds of (1) and (2). Access to various reagents as sources of (1) and (2) for subsequent metallacycle formation *via* salt elimination reactions is also explored; results include the inability to prepare a di-Grignard reagent as a source of (1), a successful *in situ* trapping Grignard reaction to generate the precursor of (2), $1,8\text{-}(Me_3SiCH_2)_2C_{10}H_6$, and an unexpected decomposition of (2) in solution to form the dianion, $[CHSiMe_2C(SiMe_3)C_{10}H_6]^{2-}$ which has been structurally authenticated by two *X*-ray structure determinations. Some of this chemistry has appeared in a preliminary communication.[9]



(1; R = H)
(2; R = $SiMe_3$)
(3; R = Ph)



(5)



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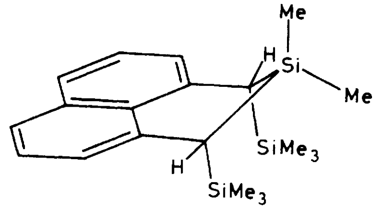

(6)

Surprisingly the O-centred isoelectronic analogue of (1) has received little attention and its chemistry appears to be different compared to the related dianions derived from catechol and 2,2′-dihydroxybiphenyl. For example, in $[Zr(1,8\text{-}O_2C_{10}H_6)_2(\eta\text{-}C_5H_5)_2]^{2-}$ monodentate ligand bonding is proposed,[10] in contrast to chelation in zirconocene compounds of $o\text{-}O_2C_6H_4{}^{2-}$ and $(2\text{-}OC_6H_4)_2{}^{2-}$ and presumably it is the small ‘ bite ’ of the naphthalene diolate that accounts for this dissimilarity. The expected similar small bite of (1) and (2) is likely to favour unusual chemistry and bonding characteristics.

Results and Discussion

Recent success in the synthesis of the benzylic type di-Grignard reagents from 1,2-bis(chloromethyl)benzene[11] and 2,2′-bis(chloromethyl)biphenyl[12] inspired us to investigate

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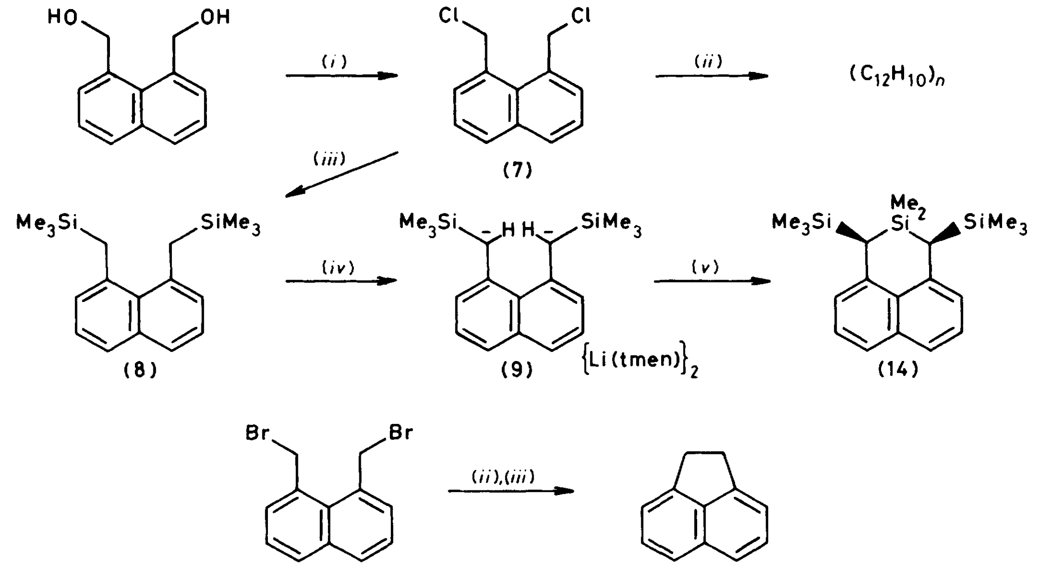
† (2,2-Dimethyl-3-trimethylsilyl-2,3-dihydro-2-silaphenalene-1,3-diyl)bis[(*NNN′N′*-tetramethylethylenediamine)lithium].

Supplementary data available (No. SUP 23745, 28 pp.): structure factors, H-atom co-ordinates, thermal parameters, molecular geometry of the β phase. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

Non-S.I. unit employed: 1 mmHg = (101 325/760) Pa.



Scheme 1. (*i*) Concentrated $HCl-H_2SO_4$; (*ii*) Mg,thf; (*iii*) Mg,thf,$SiMe_3Cl$; (*iv*) Li(tmen)Bu^n in hexane; (*v*) $SiMe_2Cl_2$-hexane

the likelihood of forming such a reagent for the closely related compound 1,8-bis(chloromethyl)naphthalene. However, using the same optimum conditions for these Grignard syntheses no activity was evident. The competing reaction is the formation of a thf-insoluble oligomer (thf = tetrahydrofuran) which suggests the lack of activity is not a consequence of the closer proximity of halogens in the present case allowing a more facile intramolecular elimination of $MgCl_2$. (Attempts to inhibit intermolecular coupling by higher dilution than that required for syntheses of the above di-Grignard reagents were unsuccessful, for projected di-Grignard concentrations down to 0.03 mol dm^{-3}.) In contrast, the competing reaction for the dibromide compound is formation of the intramolecular cyclization product, acenaphthylene (Scheme 1), the same reaction pathway as that noted for the reaction of 2,2′-bis(bromomethyl)biphenyl to yield 9,10-dihydrophenanthrene.[12] Intra- *versus* inter-molecular coupling reactions for dibromides and dichlorides respectively has been attributed to both kinetic effects (leaving group capabilities of $X^{\cdot}$) and variation in bond energies.[11,12]

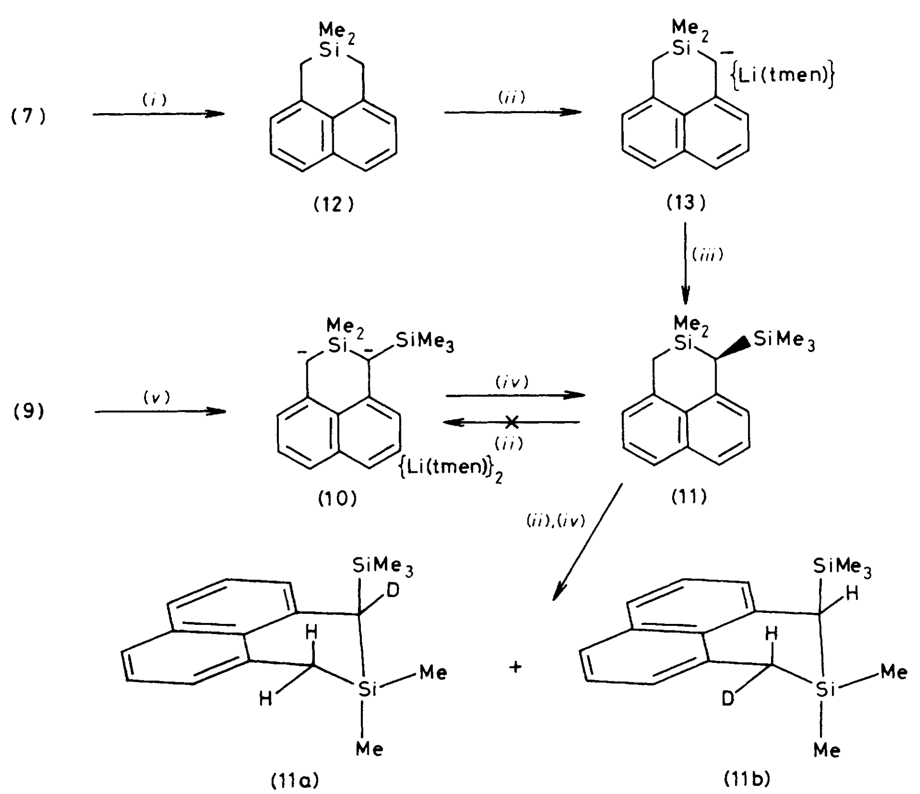
Another possible class of compound as a reagent leading to the dianion (1) is lithium alkyls. These have been investigated by several groups and the reactions investigated include that of 1,8-$(BrCH_2)_2C_{10}H_6$ with LiPh which yielded the elimination product acenaphthylene,[13] and the metallation of 1,8-$Me_2C_{10}H_6$ with Li(tmen)Bu^n (tmen = *NNN′N′*-tetramethylethylenediamine), where the product was exclusively the monolithio-species even when the organic substrate was treated with a large excess of Li(tmen)Bu^n for several days.[14] Resistance of polymethylated naphthalenes in general to di- and poly-metallation using Li(tmen)Bu^n has been explained by proposing that the removal of the second proton is more difficult because of charge density delocalization on formation of the monoanion, and the electron-releasing properties of methyl substituents.[15] An additional factor in the case of 1,8-dimethylnaphthalene may be a steric effect whereby the bulky (tmen)$LiCH_2^-$ moiety of the monoanion may impose steric constraints for metallation of the adjacent methyl group. However, for a considerably stronger base, Na(tmen)-(n-C_5H_{11}), access to the dianion (1) has been achieved, but only with excess metallating agent (3.5—4.0 mol equiv.[16]) and in consequence the reaction is of limited synthetic utility for the preparation of transition metal alkyls.

A Grignard *in situ* trapping reaction of (7) with $SiMe_3Cl$ afforded 1,8-$(Me_3SiCH_2)_2C_{10}H_6$ (8) in high yield, while the same reaction for the dibromide compound still favoured the intramolecular cyclization product, acenaphthylene. Compound (8) was found to react with Li(tmen)Bu^n, under conditions that have been utilized for monolithiation of 1,8-dimethylnaphthalene, to yield a red crystalline complex, (9). Success of dilithiation in this case possibly reflects the increase in thermodynamic acidity of $R^-CH_2SiMe_3$ (R = aryl) compared with R^-CH_3, off-setting the decrease in acidity on monolithiation.[17] Moreover, attempts selectively to monolithiate (8) using Li(tmen)Bu^n resulted in a low yield of the dilithio-species, as found in lithiation of α,α′-bis(trimethylsilyl)-*o*-xylene, although in that case monolithiation was achieved using the newly developed reagent, n-butyl(pentamethyldiethylenetriamine)lithium.[18]

Complex (9) is a potential source of the dianion $[1,8\text{-}(Me_3SiCH)_2C_{10}H_6]^{2-}$ (2), of interest for several reasons. These include the possibility of diastereoisomers for the derived heterocycles by virtue of the *peri*-carbon atoms being chiral, good solubility properties, simple n.m.r. spectra associated with the $^-SiMe_3$ groups, and the prospect of enhancement of metal alkyl stability *via* $^-SiMe_3$ steric protection of the metal centre.

In hexane (9) decomposes, with the loss of one equivalent of CH_4, to yield a novel silicon-heterocycle-containing dicarbanion complex, $[\{Li(tmen)\}_2\{\overline{CHSiMe_2C(SiMe_3)C_{10}H_6}\}]$ (10), a reaction that possibly originates from release of steric compression between the two CH substituent groups. Although an *X*-ray structure determination of (9) was considered desirable to add credence to this suggestion, all crystals examined were found to be unsatisfactory. However, the structures of related dianions, those in $[\{Li(tmen)\}_2\{o\text{-}(Me_3SiCH)_2C_6H_4\}]$[18] and $[\{Li(tmen)\}_2\{(2\text{-}Me_3SiCHC_6H_4)_2\}]$,[19] have been established and show a trigonal geometry at C_α, with the trigonal plane coplanar with an aromatic plane. For a similar structure of the *peri*-carbon atoms in (9), a gross distortion, of the type found in benzo[*c*]phenanthrene,[20] would need to be invoked and if so it may be the relief of such a distortion that is the impetus for the molecular transformation (9) ⟶ (10).

Conversion of (9) to (10) is sufficiently slow (*ca.* 6 d for completion) to allow interception of (9), in this case with



Scheme 2. (*i*) Mg,thf,$SiMe_2Cl_2$; (*ii*) Li(tmen)Bu^n in hexane; (*iii*) $SiMe_3Cl$-hexane; (*iv*) HCl-H_2O or DCl-D_2O; (*v*) hexane, 6 d

$SiMe_2Cl_2$ to yield the *meso*-siline (14), although in low yield. The n.m.r. spectra of (14) indicate the presence of non-equivalent siline silicon methyl groups and only one type of trimethylsilyl group, establishing it to be the *meso*-isomer. In a related compound, (4), formed from the dianion (3), in turn derived from alkali metal ring cleavage of *cis*- or *trans*-9,10-diphenylacenaphthene, the configuration is also *meso*, again based on n.m.r. data.[21] Increase in heteroatom size for 2,3-dihydro-2-metallaphenalenes will, by geometrical requirements, cause the heteroatom to reside further out of the plane defined by the extension of the C_{12} moiety, assuming the aromatic carbon atom framework to be inflexible. This effect is demonstrated in the structure of the thi-ine, 1,8-$(CH_2SCH_2)C_{10}H_6$.[22] N.m.r. data for (14) are consistent with fluxional behaviour in solution or a rigid molecule of possible envelope conformations (5) and (6) of which (6) can be precluded because of an unfavourable close approach of the bulky $^-SiMe_3$ groups. (No significant ^1H n.m.r. temperature dependence was evident in the range −80 to +120 °C.) Molecular mechanics calculations for the *cis* isomer of $CHMeOCHMeC_{10}H_6$ suggest that it exists predominantly with the methyls in equatorial positions whereas for the *trans* isomer, fluxional behaviour is postulated.[7]

Quenching the rearranged lithium alkyl with aqueous HCl afforded the monosilylated siline (11), the same product as that prepared by derivatization of the monolithiated siline (13), as a $^-SiMe_3$ adduct. Success of the latter route to (11) depends on the ability selectively to monolithiate (12) with Li(tmen)Bu^n, and the synthesis of (12), in high yield, *via* an *in situ* trapping Grignard reaction of (7) with $SiMe_2Cl_2$ (Scheme 2) for which the potentially competing oligomerization reaction is possibly attenuated because of the close proximity of the reaction sites favouring an intramolecular heterocycle formation. In contrast, the same reaction involving the flexible molecule $(2\text{-}ClCH_2C_6H_4)_2$ yielded both the monomeric heterocycle and oligomers.[12] A compound isomeric to (12), 2,3-dihydro-1,1-dimethyl-1-silaphenalene has been prepared by a similar *in situ* reaction involving 1-Br-8-$(ICH_2CH_2)C_{10}H_6$.[23] It is noteworthy that in the present case it appears that use of other than the dichloride (7) will result in formation of acenaphthylene.

N.m.r. data of (11) suggest a rigid envelope conformation; the *peri*-carbon protons exhibit an ABX pattern with coupling of X to only one AB proton [Figure 1(*a*)], W-type coupling, and the methyl groups attached to the heterocyclic silicon atom are non-equivalent. Irradiation of the X part of the spectrum, a doublet, at τ 7.9 simplified the ABX pattern to an AB quartet. Furthermore, the ABX pattern is unperturbed within the temperature range −80 to +180 °C and of the two possible isomers, the one with the $^-SiMe_3$ group pseudo-axial is more likely since the bulky substituent would be in a less crowded environment.

Although the dianion in (10) is readily accessible *via* decomposition of the Li(tmen)Bu^n generated anion, (2), attempts to prepare it directly by metallation of (11) using the same conditions as for the synthesis of (2) were unsuccessful. Deuterium-labelling experiments clearly show only one equivalent of deuterium to be incorporated. Hydrogen-1 n.m.r. spectra of the methylene/methine region [Figure 1(*b*)] suggest the formation of two deuteriated species (11a) and (11b), in an approximate ratio 1 : 2. Compound (11b) arises from lithiation and subsequent deuteriation at the position of the expected greatest proton acidity and accounts for the AB pattern in Figure 1(*b*). The singlets at τ 7.94 and 7.42 have been assigned to those of the isomer in which the deuterium is *trans* to $SiMe_3$. The *trans* arrangement for a deuterium at the methylene carbon is the one expected on steric and mechanistic considerations. Selective monolithiation for (11) [and (12)] compared with dilithiation of (9)

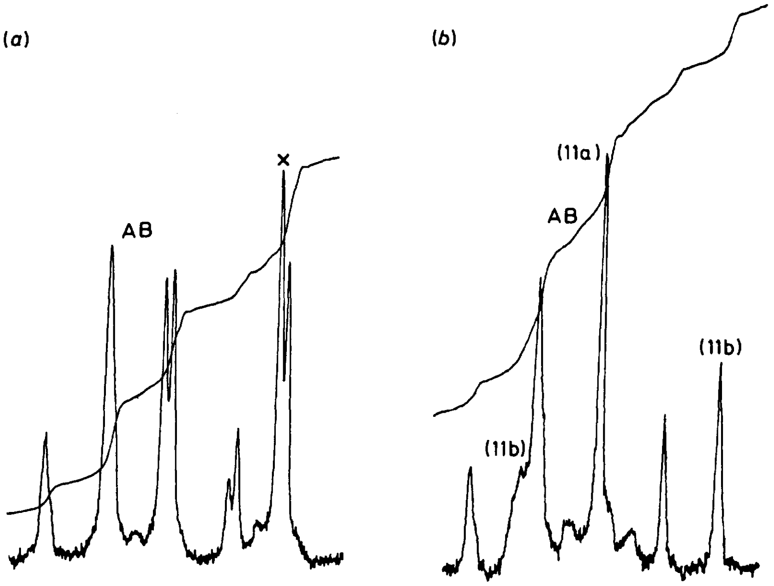


Figure 1. Hydrogen-1 n.m.r. spectra (90 MHz) recorded at 25 °C in $CDCl_3$ for the *peri*-hydrogen atoms in (*a*) $CH_2SiMe_2CH(SiMe_3)C_{10}H_6$ (11) and (*b*) monodeuteriated (11), showing resonances for the two isomers

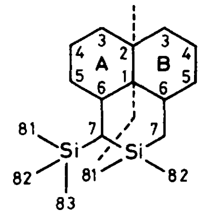
may be a consequence of the bridging $SiMe_2$ entity lacking sufficient enhancement of proton acidity to allow dilithiation, noting that for 1,8-dimethylnaphthalene there is only monolithiation.

Group 6 2,3-dihydro-2-metallaphenalenes show inversion barriers for the heterocyclic ring, increasing down the group with coalescence temperatures in the range −118 to −97.5 °C increasing in a parallel sequence.[8] However, the barrier to inversion of the related compound (12) must be inordinately small, there being no conformational rigidity for temperatures down to −118 °C. Given that the barrier to inversion is related to heteroatom size, a consequence of the larger atom residing further out of the aromatic plane, this result is surprising. In the structure of 1,8-$CH_2SCH_2C_{10}H_6$ [23] the S–C distance (1.80 Å) is shorter than the expected Si–C distances in (12) (1.90—1.95 Å) despite the ring inversion barrier being greater than in (12). However, for (12) the presence of substituents on the heteroatom is likely to effect the fluxional behaviour.

No temperature dependence of the ^1H n.m.r. spectrum of (10) was found in the range −60 to +60 °C. The methyl groups of the heterocyclic silicon may in principle be non-equivalent, either by considering a folding of the $Si(C_{methylene})_2$ plane relative to the aromatic plane and/or the nature of the lithium anion interaction, being of the ' contact ion-pair ' type (see structural commentary below).

Structural Commentary.—Both structure determinations establish the stoicheiometry of compound (10) to be as assigned below, and that it occurs on recrystallization from hexane in at least two crystalline polymorphs designated α and β, the α form predominating in the present preparation and resulting in a structure determination of greater precision. As the resulting stereochemistries in each of the two polymorphs are different we discuss them separately.

α *Form.* One formula unit of the complex comprises the asymmetric unit in a structure which, although non-centrosymmetric, nevertheless contains equal numbers of enantiomorphs by virtue of the presence of symmetry elements derived from mirror planes. The unit-cell array is depicted in Figure 2(*a*), the axis of projection lying approximately through the dianion plane; for the sake of clarity in presentation the molecular projection omits the tmen moieties so that the disposition of the lithium atoms relative to the dianion may be seen. The atom numbering for the skeletal atoms is shown below, with hydrogen atoms labelled accordingly, suffixed a, b, c where required.



The dianion of the structure is novel, and although considered in isolation initially for the sake of convenience, cannot be divorced in this complex from its interaction with the lithium atoms. It comprises a naphthalene ring system fused through the 1,8-positions to a six-membered heterocyclic ring containing a silicon atom at its apex and incorporating the immediate substituent atoms into the conjugated system as evidenced by the C(6)–C(7) distances (Table 1). Although C(1)–C(2) is long and C(3)–C(4) short, as in most naphthalene systems, this is not carried through to a short C(5)–C(6) distance, presumably because of the extension of conjugation to the C(7) atoms and the resulting delocalization of negative charge from C(7) to C(5), an interpretation reinforced by the enlargement of the A and B ring angles at C(5) and a diminution at C(6). In consequence, association of the lithium atoms with C(5) and C(7) might be expected, as is observed. The naphthalene ring system, with the two 1,8-substituent atoms defines a tolerably planar system (σ = 0.04 Å), from which the heterocyclic silicon atom deviates by −0.54 Å and the exocyclic substituent silicon by −0.24 Å. Methyl substituent carbon atoms (81A, 82A, 83A, 81B, 82B) deviate by 1.09, −1.87, −0.31, −2.41, 0.26 Å respectively;

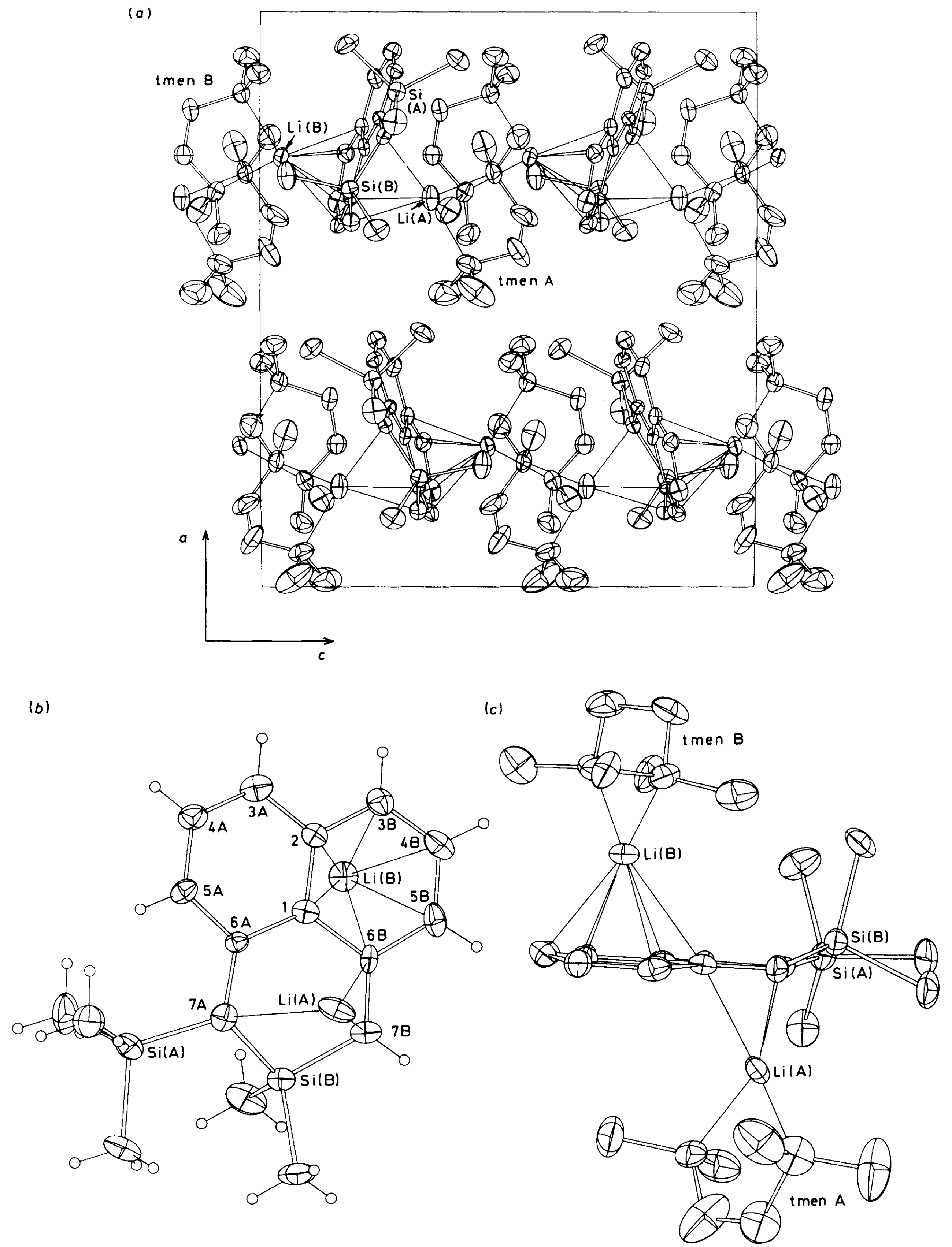


Figure 2. (*a*) Unit-cell contents of the α phase of (10) projected down *b*; 20% thermal ellipsoids are shown for the non-hydrogen atoms. Contacts from the lithium atoms to the aromatic system are shown as single lines. (*b*) Projection of the dianion of the α phase and its associated lithium atoms normal to the aromatic plane. Hydrogen atoms are shown as spheres of radius 0.1 Å. (*c*) The full ' molecule ' of the α phase projected through the dianion

Table 1. Molecular non-hydrogen geometry, distances (Å) and angles (°), for the α phase of (10); the two values in each entry are for sections A,B

C(1)–C(2)	1.45(1)	C(6)–C(1)–C(6)	121.6(7)	C(82)–Si–C(83)	104.1(4)
C(1)–C(6)	1.48(1)	C(6)–C(1)–C(2)	119.3(7), 119.1(7)	Li–N(1)–C(1)	106.8(9), 104.8(7)
C(2)–C(3)	1.41(1), 1.41(1)	C(1)–C(2)–C(3)	120.2(7), 120.2(8)	Li–N(1)–C(11)	105.7(7), 119.3(7)
C(3)–C(4)	1.35(1), 1.36(2)	C(3)–C(2)–C(3)	119.6(8)	Li–N(1)–C(12)	115.3(7), 102.9(6)
C(4)–C(5)	1.39(1), 1.38(1)	C(2)–C(3)–C(4)	120.2(8), 121.2(8)	C(1)–N(1)–C(11)	110.8(9), 108.8(7)
C(5)–C(6)	1.41(1), 1.43(1)	C(3)–C(4)–C(5)	120.9(8), 119.4(8)	C(1)–N(1)–C(12)	111.2(10), 111.4(8)
C(6)–C(7)	1.43(1), 1.40(1)	C(4)–C(5)–C(6)	124.6(8), 125.5(8)	C(11)–N(1)–C(12)	106.8(9), 109.5(7)
C(7)–Si	1.863(7), 1.816(8)	C(5)–C(6)–C(1)	114.7(7), 114.2(7)	N(1)–C(1)–C(2)	119.5(14), 114.0(8)
Si–C(81)	1.892(10), 1.912(9)	C(5)–C(6)–C(7)	120.8(7), 122.0(7)	C(1)–C(2)–N(2)	121.0(15), 112.1(8)
Si–C(82)	1.869(10), 1.908(10)	C(1)–C(6)–C(7)	124.4(7), 123.8(7)	Li–N(2)–C(2)	104.7(9), 105.5(7)
Si–C(83)	1.882(9)	C(6)–C(7)–Si	118.4(5), 121.2(6)	Li–N(2)–C(21)	104.0(8), 105.8(7)
Li–N(1)	2.13(1), 2.12(2)	C(7)–Si–C(81)	117.7(4), 112.7(4)	Li–N(2)–C(22)	121.4(9), 115.8(7)
Li–N(2)	2.18(2), 2.08(1)	C(7)–Si–C(82)	112.0(4), 108.3(4)	C(2)–N(2)–C(21)	109.4(12), 111.3(7)
C(1)–N(1)	1.45(2), 1.45(1)	C(7)–Si–C(83)	112.6(4)	C(2)–N(2)–C(22)	106.8(11), 111.2(8)
C(2)–N(2)	1.46(2), 1.46(1)	C(81)–Si–C(82)	106.8(4), 103.1(4)	C(21)–N(2)–C(22)	109.7(11), 107.2(8)
C(1)–C(2)	1.31(3), 1.46(2)	C(81)–Si–C(83)	102.3(4)		
N(1)–C(11)	1.45(1), 1.45(1)				
N(1)–C(12)	1.46(1), 1.49(1)				
N(2)–C(21)	1.43(2), 1.45(1)				
N(2)–C(22)	1.45(2), 1.47(1)				

Li–C(aromatic) interactions

Li(A)–C(7A,B)	2.46(2), 2.35(1)
Li(B)–C(2,3B,4B,5B)	2.43(1), 2.34(2), 2.40(2), 2.43(2)
C(A7)–Si(B)	1.832(8)
C(A7)–Si(B)–C(7B,81B,82B)	101.5(4), 113.9(4), 117.4(4)

the last two (81B, 82B) essentially constitute axial and equatorial substituent respectively atoms on the heterocyclic ring. The axial methyl substituent is disposed on the opposite side of the ring ' plane ' to Li(A), which lies in close proximity to C(7B) [2.35(1) Å] and also at slightly longer distances to C(6B,7A) [2.51(1), 2.46(2) Å]. Li(A) lies 1.90 Å out of the aromatic ring plane defined above. Li(B) lies −1.97 Å out of the plane on the opposite side of the plane to Li(A) and in close proximity to all naphthalene B ring atoms, being only slightly displaced from directly above the ring centroid [Figure 2(*b*)]. Li(B)–C(1—6B) distances are 2.49(1), 2.43(1), 2.34(2), 2.40(2), 2.43(2), 2.49(1) Å respectively; the disposition of both lithium atoms in the same half of the ligand presumably arises in consequence of enhanced π-delocalization to C(6B)–C(7B), in turn enhancing the negative charge at C(5B), while displacement of Li(A) (together with its bulky tmen environment) toward C(7B) is presumably a consequence of the disposition of substituent bulk on the A side of the system. The association of the tmen units with the lithium atoms, as usual, is by chelation, with lithium nitrogen distances lying in the range 2.08(1)—2.18(2) Å; the distances for Li(A) may be somewhat longer than those for Li(B) [2.13(1), 2.18(2); *cf.* 2.12(2), 2.08(1) Å].

The structure is best described as a ' contact ion-pair ' type exemplified by the structures of [{Li(tmen)}$_2${*o*-(Me$_3$SiCH)$_2$-C$_6$H$_4$}],[18] [{Li(tmen)}(CPh$_3$)],[24] and [{Li(tmen)}$_2$(C$_{10}$H$_8$)].[25] (Covalent Li–C bonding with bidentate tertiary amines present is limited to compounds void of Li–C(aromatic) contacts, *viz.* [{Li(tmen)}{CH(SiMe$_3$)$_2$}] [17] and [(tmen)Li{S(CH$_2$)$_3$SC(Me)}$_2$Li(tmen)].[26]) The lithium environment in the latter, possessing an η^6 contact to the aromatic moiety, is similar to Li(B) in the present structure [Li–C 2.27(1)—2.66(1) Å].[25]

Although *sp*^{2} hybridization at C(7) would tend to dictate a planar heterocycle, the Si resides out of the aromatic plane with an associated fold angle, the dihedral angle between Si,C(7A),C(7B) and the associated C$_5$ plane, of 27.0° (*cf.* 31° in 1,8-SCH$_2$C$_{10}$H$_6$CH$_2$).[22] It may be the elongation of C(1)–C(6) (1.48 Å) that results from optimization of accommodating the heteroatom within the plane of the ring, and *sp*^{2} hybridization at C(7).

β *Form*. Regrettably the precision of this determination is lower than that of the α form and serves only to define general atom disposition. Only atom co-ordinates and Figures are given in the main text. Again, one formula unit comprises the asymmetric unit of the structure; a cell projection down the unique axis is given in Figure 3(*a*), with a molecular projection similar to that of Figure 2(*b*), but without thermal ellipsoids.

The methyl substituent disposition relative to the fused ring system is the same as that of the α form. Silicon atom dispositions (δ) are to either side of the aromatic plane defined by the ten naphthalene carbon atoms (σ = 0.05 Å). Deviations of Si(A,B) are 0.34 and −0.63 Å, while deviations of C(7A,B) are 0.24 and −0.42 Å, and δC(81,82B) are −2.42 and 0.08 Å. Those of C(7A,B), to opposite sides of the aromatic plane, are prevalent for bulky substituents in the 1,8-positions of naphthalene.[1,2,27]

Again, the two lithium atoms are associated with the dianion, one above the heterocyclic ring, opposite the axial methyl substituent and in proximity to C(6,7;A,B). Li(A)–C(6A,6B,7A,7B) are 2.49(5), 2.39(6), 2.24(5), and 2.64(5) Å, and the deviation of Li(A) from the aromatic plane is 1.85 Å. Li(B) lies on the opposite side of the plane (deviation −1.99 Å), but instead of lying over the fused naphthalene B ring it lies outside it, associated with C(5B,6B,7B) [respective distances 2.17(4), 2.19(5), and 2.12(6) Å]. As for the α phase the structure is of the ' contact ion-pair ' type. An electrostatic model, the metal interacting with the expected highest electron density positions, is inadequate for predicting the structure.[25] This is clearly demonstrated in the present structures in which the position of lithium contacts varies considerably and possibly depends on other factors such as steric effects and crystal packing forces.

Experimental

General Procedures.—Operations involving the Grignard *in situ* reactions and the use of lithium alkyls were carried out under a dry and oxygen-free argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from Na–benzophenone (diethyl ether), LiAlH$_4$ (pentane and thf), KOH (tmen), and CaH$_2$ (hexane) under a dinitrogen atmosphere prior to use.

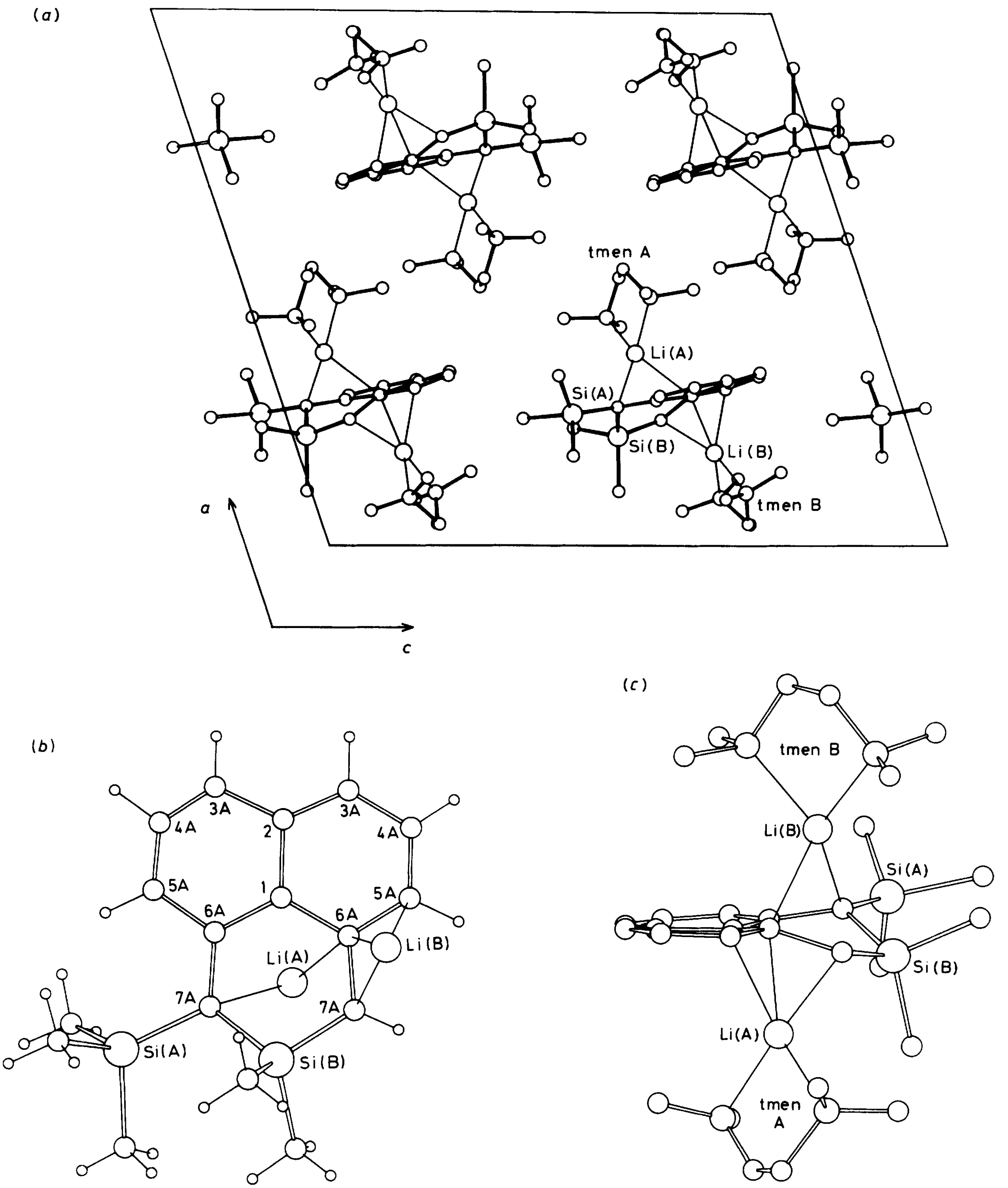


Figure 3. (*a*) Unit-cell contents of the β phase projected down *b*. (*b*) Projection of the dianion of the β phase and its associated lithium atoms normal to the aromatic plane. (*c*) Projection of the full ' molecule ' of the β form through the dianion plane

Physical and Analytical Measurements.—Elemental analyses were performed by the Canadian Microanalytical Laboratory and the Australian Mineral Development Laboratories. I.r. spectra were obtained from KBr disc dispersions or thin films between KBr plates on a Perkin-Elmer 283 spectrometer. Hydrogen-1 n.m.r., carbon-13 n.m.r., and mass spectra were recorded on Hitachi-Perkin-Elmer R-24B (60 MHz), Brüker WP-80, and Brüker HP-4986 spectrometers respectively.

Synthesis of 1,8-*Bis(chloromethyl)naphthalene*, (7).—Concentrated sulphuric acid (40 cm^3) was added slowly to stirred ice-cooled concentrated hydrochloric acid (80 cm^3). 1,8-Bis(hydroxymethyl)naphthalene (10 g, 53 mmol), prepared according to the literature procedure,[28] was then added and the mixture stirred at room temperature for 12 h, whereupon the solid was collected, washed with water (2 × 30 cm^3) and recrystallized from hexane (150 cm^3) to afford colourless plates, m.p. 88—90 °C. Yield 8.35 g, 70% (Found: C, 64.2; H, 4.4. Calc. for $C_{12}H_{10}Cl_2$: C, 64.0; H, 4.5%). ^{1}H N.m.r. ($CDCl_3$), τ 4.75 (s, 4 H, CH_2Cl), 2.5 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. (C_6D_6, ^1H decoupled), δ 48.6 (s, CH_2Cl), 129.8, 133.5, 136.4 (3 C, $C_{10}H_6$), 125.9, 132.1, 133.1 (3 CH, $C_{10}H_6$); mass spectrum *m/e* 224 (P)$^+$, 191 ($P - Cl$)$^+$, 155 ($P - 2Cl$)$^+$; i.r. (KBr), 3 050w, 1 610w, 1 540m, 1 485m, 1 455m, 1 390w, 1 290m, 1 260m, 1 225m, 1 180w, 1 165m, 1 130m, 1 040w, 1 005m, 970w, 910w, 905w, 840s, 820w, 780s, 695m, 680s, 645m, 605w, 590m, 545m, 520m, 490w, 470w, and 360m cm^{-1}.

Synthesis of 1,8-*Bis*(*trimethylsilylmethyl*)*naphthalene*, (8).—To a suspension of magnesium powder (1.5 g, 61.7 mmol) in thf (10 cm^3) was added 1,2-dibromoethane (0.2 cm^3), and the mixture warmed until evolution of ethylene was evident, whereupon the mixture was stirred for 5 min. The thf was replaced by fresh thf (10 cm^3) and $SiMe_3Cl$ added (8.4 cm^3, 66.2 mmol) prior to the slow addition of compound (7) (5 g, 22.2 mmol) in thf (40 cm^3) at such a rate as to maintain the temperature close to 40 °C. After addition was complete, stirring was continued for 15 h at room temperature. Solvent was then removed *in vacuo* and the residue extracted with hexane (100 cm^3). The filtrate was washed with dilute HCl (20 cm^3), dried (Na_2CO_3), and concentrated. Distillation afforded a colourless liquid, b.p. 120 °C (0.5 mmHg). Yield 6.2 g, 93% (Found: C, 72.8; H, 10.2. Calc. for $C_{18}H_{28}Si_2$: C, 71.9; H, 9.4%). ^1H N.m.r. ($CDCl_3$), τ 10.1 (s, 18 H, $SiMe_3$), 7.3 (s, 4 H, CH_2), 2.8 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. ($CDCl_3$, ^1H decoupled), δ −1.3 (s, $SiMe_3$), 29.7 (s, CH_2), 125.0, 127.1, 128.5 (3 CH,$C_{10}H_6$), 131.7, 136.7, 138.2 (3 C,$C_{10}H_6$); mass spectrum *m/e* 300 (P)$^+$, 212 ($P - SiMe_3$)$^+$, 152 ($P - 2SiMe_3$)$^+$; i.r. (film), 3 080w, 2 970m, 2 910w, 1 580m, 1 420w, 1 380w, 1 340w, 1 260s, 1 170m, 1 080w, 1 025m, 970s, 850s, 770s, and 695m cm^{-1}.

Synthesis of 2,2-*Dimethyl*-2,3-*dihydro*-2-*silaphenalene*, (12).—The same procedure and quantities as for the preparation of (8) were used but with $SiMe_2Cl_2$ (5.6 cm^3, 44.0 mmol), and the hexane extract on concentration yielded a colourless solid which was crystallized from methanol as needles, m.p. 67 °C. Yield 3.5 g, 75% (Found: C, 79.4; H, 7.55. Calc. for $C_{14}H_{16}Si$: C, 79.2; H, 7.6%). ^1H N.m.r. ($CDCl_3$), τ 10.0 (s, 6 H, $SiMe_2$), 7.6 (s, 4 H, CH_2), 2.6 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. ($CDCl_3$, ^1H decoupled), δ −3.7 (s, $SiMe_2$), 23.2 (s, CH_2), 125.5, 126.8, 128.8 (3 CH,$C_{10}H_6$), 132.5, 135.4, 136.5 (3 C,$C_{10}H_6$); mass spectrum *m/e* 356 (P)$^+$, 268 ($P - SiMe_4$)$^+$; i.r. (KBr), 3 000m, 1 600w, 1 580s, 1 505m, 1 450w, 1 440w, 1 410w, 1 370m, 1 355m, 1 270s, 1 250s, 1 180m, 1 170s, 1 150m, 1 140m, 1 100w, 1 030m, 1 000s, 970m, 850s, 800s, 770s, and 640m cm^{-1}.

Reaction of (7) *or* 1,8-*Bis*(*bromomethyl*)*naphthalene with Magnesium.*—Details for these reactions are identical to those described for the di-Grignard synthesis of 1,2-bis(chloromethyl)benzene [11] and 2,2′-bis(chloromethyl)biphenyl.[19] In the case of (7), a white precipitate formed during the course of the reaction, while for the dibromide the solution remained free from organic precipitates and on work-up the product was found to be acenaphthylene. Filtration of the attempted di-Grignard syntheses solutions, and quenching 1-cm^3 aliquots with 0.1 mol dm^{-3} HCl and titrating with 0.1 mol dm^{-3} NaOH indicated no di-Grignard activity. Moreover, the same reactions for the dibromide in the presence of $SiMe_3Cl$ or $SiMe_2Cl_2$ still gave the intramolecular cyclization product. 1,8-Bis(bromomethyl)naphthalene was prepared from 1,8-bis(hydroxymethyl)naphthalene according to the literature procedure.[29]

Synthesis of [{Li(tmen)}$_2${1,8-($CHSiMe_3$)$_2C_{10}H_6$}] (9).—To a cooled (0 °C) solution of $LiBu^n$ in hexane (5 cm^3, 1.73 mol dm^{-3}, 8.6 mmol) was added tmen (1.3 cm^3, 8.6 mmol) dropwise with stirring, followed by (8) (1.35 g, 4.5 mmol) and the red solution left for 1 h at room temperature. Solvent was then removed *in vacuo* until onset of crystallization. After 15 min at room temperature, residual solvent was removed and the red needles washed with pentane (3 × 5 cm^3) and dried *in vacuo*, m.p. 50—52 °C. Yield 2.05 g, 83%; ^1H n.m.r. (C_6D_6), τ 9.60 (s, 18 H, $SiMe_3$), 8.35 (s, 8 H, NCH_2), 8.23 (s, 24 H, NCH_3), 6.55 (s, 2 H, CH), 3.0—4.2 (m, 6 H, $C_{10}H_6$). Compound (9) decomposes in solution to give (10) (see below) and no satisfactory ^{13}C n.m.r. spectrum of (9) was obtained.

Synthesis of [{Li(tmen)}$_2${$\overline{CHSiMe_2C(SiMe_3)C_{10}H_6}$}] (10) *from* (9).—The initial red solution for the preparation of (9) was kept at room temperature for six days during which red prisms deposited. These were washed with pentane (3 × 5 cm^3) and dried *in vacuo*, m.p. 108—110 °C (α phase). Yield 1.8 g, 75%; ^1H n.m.r. (C_6D_6), τ 9.74 (s, 6 H, $SiMe_2$), 9.55 (s, 9 H, $SiMe_3$), 8.35 (s, 8 H, NCH_2), 8.26 (s, 24 H, NCH_3), 6.93 (s, 1 H, CH), 3.5—4.7 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. (C_6D_6, ^1H decoupled), δ 3.7 (s, $SiMe_3$), 8.1 (s, $SiMe_2$), 27.7 (s, CH), 45.2 (s, NCH_3), 56.9 (s, NCH_2), 97.5, 104.5, 116.0 (3 CH, $C_{10}H_6$), 142.2, 152.6, 157.0 (3 C,$C_{10}H_6$).

Synthesis of 2,2-*Dimethyl*-1-*trimethylsilyl*-2,3-*dihydro*-2-*silaphenalene*, (11).—To a mixture of (10) and hexane, prepared according to the above procedure was added slowly aqueous HCl (1 mol dm^{-3}, 30 cm^3). After 5 min stirring at room temperature the organic phase was separated, dried (Na_2CO_3) and the solvent removed *in vacuo* to afford a colourless liquid, b.p. 140 °C (0.5 mmHg). Yield 0.91 g, 72% (Found: C, 71.65; H, 8.65. Calc. for $C_{17}H_{24}Si_2$: C, 71.85; H, 8.5%). ^1H N.m.r. ($CDCl_3$, 90-MHz spectrum obtained on a Brüker HX-90 spectrometer), 10.15 (s, 3 H, $SiMe_2$), 10.1 (s, 9 H, $SiMe_3$), 9.7 (s, 3 H, $SiMe_2$), 8.1 (J_{BX} *ca.* 0, J_{AX} 2.5, X part of ABX, CH), 7.9 (J_{AB} 17.0, J_{AX} *ca.* 0 Hz, AB part of ABX, CH_2), 2.7 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. ($CDCl_3$ ^1H decoupled), δ −2.0 (s, $SiMe_2$), −0.8 (s, $SiMe_2$), 0.0 (s, $SiMe_3$), 2.10 (s, CH_2), 26.0 (s, CH), 125.1, 125.8, 127.0, 129.2, 129.4 (CH,$C_{10}H_6$), 135.6, 135.8, 138.9 (3 C,$C_{10}H_6$); mass spectrum *m/e* 285 (P)$^+$, 197 ($P - SiMe_3$)$^+$; i.r. (film), 3 060m, 2 980s, 2 900m, 1 730m, 1 575s, 1 505m, 1 400m, 1 370m, 1 330w, 1 255s, 1 180m, 1 160m, 1 130w, 1 100w, 1 030s, 990w, 840s, 770s, and 690m cm^{-1}.

Synthesis of [{Li(tmen)}($\overline{CHSiMe_2CH_2C_{10}H_6}$)] (13) *and the Trimethylsilyl Derivative*, (11).—To a cooled (0 °C) solution of $LiBu^n$ in hexane (10 cm^3, 1.73 mol dm^{-3}, 17.5 mmol) was added tmen (2.8 cm^3, 18.7 mmol) slowly with stirring, followed by (12) (3.5 g, 16.4 mmol). Red needles precipitated during 5 min at room temperature which were then washed with pentane (3 × 5 cm^3), m.p. 94—96 °C. Yield 4.3 g, 78%; repeated attempts to obtain n.m.r. data were unsuccessful. To a mixture of (13) and hexane (50 cm^3) at 0 °C, $SiMe_3Cl$ (1.78 g, 16.4 mmol) was added slowly with stirring. Stirring was continued for 2 h at room temperature whereupon aqueous HCl (2 mol dm^{-3}, 25 cm^3) was added. The organic layer was separated, dried, and concentrated. Column chromatography [silica gel, 60—120 mesh, hexane–CH_2Cl_2 (95 : 5) eluant] afforded (11) as a colourless liquid (2.25 g, 62%).

Lithiation of (11).—To a cooled (0 °C) solution of $LiBu^n$ in hexane (4 cm^3, 1.7 mol dm^{-3}, 8.8 mmol) was added tmen (1.1 cm^3, 8.8 mmol) slowly with stirring, followed by (11) (1.0 g, 3.5 mmol) and the resulting red solution left for 12 h at room temperature. Quenching with DCl in D_2O (8 mol dm^{-3}, 2 cm^3, 0.16 mmol), and work-up as for the synthesis of

Table 2. Non-hydrogen atomic co-ordinates (α phase)

	Section A			Section B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Li	0.679 5(10)	0.541 8(8)	0.343 5(8)	0.747 3(9)	0.393 5(9)	0.043 4(9)
C(1)	0.763 6(5)	0.454 3(5)	0.209 4(4)			
C(2)	0.800 1(5)	0.366 5(5)	0.205 0(5)			
C(3)	0.883 3(6)	0.353 7(6)	0.232 2(6)	0.753 2(7)	0.293 8(5)	0.172 5(6)
C(4)	0.928 8(5)	0.422 8(6)	0.264 6(6)	0.671 0(7)	0.302 0(6)	0.154 0(7)
C(5)	0.895 3(5)	0.507 8(5)	0.269 8(6)	0.634 6(5)	0.384 8(6)	0.158 9(6)
C(6)	0.814 7(5)	0.530 2(5)	0.241 2(5)	0.676 0(4)	0.465 6(5)	0.182 4(5)
C(7)	0.785 5(5)	0.619 4(5)	0.249 3(5)	0.635 6(5)	0.547 3(5)	0.181 3(6)
Si	0.861 68(—) *	0.709 0(1)	0.273 8(2)	0.692 8(2)	0.650 8(1)	0.181 7(2)
C(81)	0.916 8(6)	0.707 4(6)	0.394 4(7)	0.714 7(7)	0.694 1(6)	0.054 3(6)
C(82)	0.943 1(6)	0.715 0(6)	0.178 3(7)	0.624 3(6)	0.740 8(6)	0.235 9(7)
C(83)	0.813 7(7)	0.822 6(7)	0.272 8(7)			
tmen ligands						
C(1)	0.647 9(10)	0.459 6(13)	0.530 0(10)	0.831 4(7)	0.405 2(7)	−0.137 4(7)
N(1)	0.720 5(5)	0.474 3(5)	0.469 7(5)	0.857 9(5)	0.402 1(5)	−0.037 5(5)
C(11)	0.777 8(8)	0.534 0(8)	0.516 7(8)	0.919 6(7)	0.333 4(7)	−0.027 2(7)
C(12)	0.764 7(10)	0.391 6(7)	0.452 3(8)	0.892 9(5)	0.488 4(7)	−0.006 2(8)
C(2)	0.581 5(12)	0.507 3(11)	0.515 7(12)	0.753 0(8)	0.450 8(7)	−0.152 2(6)
N(2)	0.562 4(5)	0.542 8(7)	0.420 4(7)	0.688 7(5)	0.417 9(5)	−0.087 5(5)
C(21)	0.515 2(9)	0.622 5(10)	0.430 7(13)	0.657 3(6)	0.333 2(7)	−0.119 6(8)
C(22)	0.513 5(9)	0.476 0(12)	0.370 8(10)	0.618 5(7)	0.479 5(8)	−0.083 6(7)

* Defines origin.

Table 3. Non-hydrogen atomic co-ordinates (β phase)

	Section A			Section B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Li	0.358(2)	0.377(5)	0.594(2)	0.175(2)	0.247(5)	0.669(2)
C(1)	0.281(1)	0.488(3)	0.663(1)			
C(2)	0.305(1)	0.562(3)	0.731(1)			
C(3)	0.310(1)	0.721(3)	0.728(1)	0.325(2)	0.470(4)	0.785(1)
C(4)	0.296(2)	0.787(3)	0.672(2)	0.319(2)	0.317(4)	0.782(2)
C(5)	0.279(1)	0.730(3)	0.612(1)	0.293(1)	0.248(3)	0.721(1)
C(6)	0.271(1)	0.575(3)	0.603(1)	0.281(1)	0.325(3)	0.662(1)
C(7)	0.260(1)	0.510(3)	0.536(1)	0.237(1)	0.247(3)	0.600(1)
Si	0.245 7(5)	0.627 8(11)	0.461 1(4)	0.204 8(4)	0.334 3(9)	0.522 1(4)
C(81)	0.317(1)	0.744(3)	0.459(1)	0.103(2)	0.371(3)	0.493(1)
C(82)	0.237(2)	0.525(4)	0.380(2)	0.218(1)	0.208(3)	0.455(1)
C(83)	0.166(2)	0.756(5)	0.441(2)			
tmen ligands						
C(1)	0.518(2)	0.406(4)	0.620(2)	0.039(2)	0.156(5)	0.689(2)
N(1)	0.465(1)	0.477(2)	0.648(1)	0.089(1)	0.083(3)	0.654(1)
C(11)	0.473(2)	0.631(4)	0.643(2)	0.066(2)	0.038(5)	0.586(2)
C(12)	0.479(2)	0.455(4)	0.723(2)	0.125(2)	−0.045(4)	0.692(2)
C(2)	0.502(2)	0.254(4)	0.609(2)	0.040(2)	0.300(5)	0.686(2)
N(2)	0.427(1)	0.215(3)	0.567(1)	0.098(2)	0.386(4)	0.698(2)
C(21)	0.426(2)	0.225(5)	0.498(2)	0.137(2)	0.403(4)	0.766(2)
C(22)	0.410(2)	0.073(5)	0.585(2)	0.087(3)	0.509(5)	0.663(2)

(11) from (10), gave a yellow oil which was subject to chromatography [hexane–CH_2Cl_2 (95 : 5)] yielding monodeuteriated (11) (gas-chromatographic mass spectrum), 0.2 g (20%). ^1H N.m.r. (90 MHz) showed two isomers to be present [see Figure 1(*b*)].

Synthesis of 2,2-*Dimethyl*-1,3-*bis*(*trimethylsilyl*)-2,3-*dihydro*-2-*silaphenalene*, (14).—To a solution of (9) (2.3 g, 4.2 mmol) in diethyl ether (50 cm^3) was added slowly $SiMe_2Cl_2$ (0.66 cm^3, 10 mmol) while maintaining the temperature at 35 °C. After stirring for 1 h at room temperature the solution was filtered and concentrated *in vacuo* to afford a yellow oil which was chromatographed [silica gel, 60—120 mesh, hexane–CH_2Cl_2 (95 : 5) eluant]. A colourless liquid was obtained which crystallized on standing (0.7 g, 5%), m.p. 62 °C (Found: C, 66.95; H, 9.35. Calc. for $C_{20}H_{32}Si_3$: C, 67.35; H, 9.05%). ^1H N.m.r. ($CDCl_3$), τ 9.90 (s, 18 H, $SiMe_3$), 9.88, 9.78 (s, 6 H, $SiMe_2$), 8.15 (s, 2 H, CH), 2.4 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. ($CDCl_3$, ^1H decoupled), δ −0.5, 2.5 ($SiMe_2$), 1.75 (s, $SiMe_3$), 24 (s, CH), 124.7, 125.5, 128.3 (3 CH,$C_{10}H_6$), 135.4, 138.3 (3 C,$C_{10}H_6$); mass spectrum *m*/*e* 360 $(P)^+$, 268; i.r. (film), 3 060w, 2 970m, 2 930w, 1 740m, 1 570m, 1 430w, 1 370w, 1 255s, 1 070m, 1 025m, 980w, 930w, 840s, 800w, 766m, and 680w cm^{-1}.

Crystallography.—Crystal data for α phase of (10). $C_{29}H_{54}N_4Li_2Si_2$, $M = 528.7$, orthorhombic, space group $P2_1cn$ (variant of $Pna2_1$, C_{2v}^9, no. 33), $a = 16.224(5)$, $b = 15.080(5)$, $c = 13.828(3)$ Å, $U = 3\,383(2)$ Å^3, $Z = 4$, $D_c = 1.04$ g cm^{-3}, $F(000) = 1\,160$, monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu_{Mo} = 1.3$ cm^{-1}, $T = 295(1)$ K.

Crystal data for β *phase of* (10). Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 19.09(2)$, $b = 9.05(1)$, $c = 20.86(3)$ Å, $\beta = 108.53(9)°$, $U = 3\,416(7)$ Å^3, $Z = 4$, $D_c = 1.03$ g cm^{-3}, $\mu_{Mo} = 1.3$ cm^{-1}.

Structure determination. Unique data sets were measured to $2\theta_{max.} = 45°$ on crystals mounted in capillaries using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ/θ scan mode, yielding 2 303 (α) and 3 203 (β) independent reflections; of these 1 261 (α) and 2 165 (β) with $I \geqslant 3\sigma(I)$ were considered 'observed' and used in 9 × 9 block-diagonal least-squares refinement, without absorption correction, after solution of the structures by direct methods. For the α phase anisotropic thermal parameters were refined for the non-hydrogen atoms; for the hydrogen atoms (x,y,z,U) were estimated and constrained, U being set at 1.25 $\bar{U}_{ii}$ (parent atom). At convergence residuals (R,R') were 0.043 and 0.047, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. For the β phase, the precision of the determination was adversely affected by the need to collect data using the available material in the form of a couple of very large flat plates, one of which was used without any attempt to reduce its size, since they were found to be fragile. Only the silicon atom thermal motion could be significantly refined anisotropically; at convergence R,R' were 0.20 and 0.18. Neutral-atom scattering factors were employed, those for the non-hydrogen atoms being corrected for anomalous dispersion (f'').[30] Computation used the *X*-RAY 76 program system[31] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Atomic coordinates are presented in Tables 2 and 3.

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