Axially Asymmetric Metal Alkyls. Part 1. Lithium Alkyls of 2,2′-Dimethylbiphenyl and its Trimethylsilylmethylated Compounds: Crystal Structures of [$\{Li(Me_2NCH_2CH_2NMe_2)\}_2\{(2\text{-}CHRC_6H_4)_2\}$] for R = H (Polymeric) and R = $SiMe_3$ (Monomeric) †

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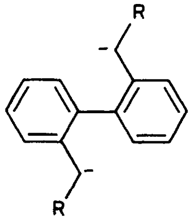
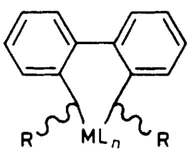
Metallation of $(2\text{-}CH_2RC_6H_4)_2$, with excess Li(tmen)Bu^n (tmen = *NNN′N′*-tetramethylethylenediamine) yields the crystalline compounds [$\{Li(tmen)\}_2\{(2\text{-}CHRC_6H_4)_2\}$][R = H (7) or $SiMe_3$ (9)] whereas for 2-methyl-2′-trimethylsilylmethylbiphenyl, although selectivity is maintained, the crystalline product is a monolithiated species. This difference has been rationalised on the basis of the results of the crystal structure determination of the lithium complexes (7) and (9). The structure of (7) is polymeric (*cf.* dimeric in benzene by ebullioscopy) with a ' metallacycle ' lithium and a lithium bridging methylene groups of different ' metallacycles ' (electron-deficient bonding): Li–C (mean) 2.30 Å; Li–C–Li (mean) 159.5, C–Li–C (mean) 106.5°. Compound (9) is best described as a ' contact ion-pair ' structure; Li–C(H)$SiMe_3$ contacts, 2.22(1) and 2.19(2) Å. Lithiation of 2-[bis(trimethylsilyl)methyl]-2′-methylbiphenyl results in the formation of (9), *via* an anionic 1,6-silyl migration.

Since the realisation of β-hydrogen elimination as a facile decomposition pathway for metal alkyl species, numerous examples of stable metal alkyls, possessing β-hydrogen free ligands, such as benzyl, have been reported. An extension of metal alkyl chemistry is that involving chelating alkyls, the derived complexes being designated metallacycles, and the chemistry is substantially different from that of open-chain analogues.[1] Recent studies on metallacycles of *o*-xylidene, $o\text{-}(CH_2)_2C_6H_4^{2-}$, clearly demonstrate that the chemistry bears little resemblance to that of the related unidentate ligand, the benzyl group.[2–4] A new class of metallacycles (2; R = H), structurally more akin to two benzyl groups attached to a metal, have featured in preliminary publications dealing with metallocene derivatives of Group 4 [5] and 5 [6] transition metals and tin(IV),[5] prepared from an organodilithium complex and/or a di-Grignard reagent by salt elimination reactions with the appropriate metal chloride. The species $(2\text{-}OC_6H_4)_2^{2-}$, which is in principle isoelectronic with $(2\text{-}CH_2C_6H_4)_2^{2-}$ (1; R = H), is well established as a bidentate ligand,[7] and like the C-centred analogue is axially asymmetric, a molecular feature that is of interest from a stereochemical and synthetic point of view.[8]

In this paper attention is focused primarily on the synthesis and characterisation of Group 1A reagents, possible precursors to metallacycles (2) (R = H or $SiMe_3$). Incorporation of trimethylsilyl groups at C_α (methylene carbon atoms) is with a view to achieving enhanced metal alkyl stability *via* protective binding which is invariably associated with such bulky groups, and the likelihood of increased solubility, simple n.m.r. spectra, and the prospect of several diastereoisomers by virtue of one or more chiral centres present. Included here is the isolation of three crystalline lithium alkyls and crystal structures of two of these, and an unusual 1,6-silyl migration; the synthesis of the lithium complex containing (1; R = H) has appeared in a preliminary communication.[5] Subsequent papers will initially be concerned with synthesis, structure, and reactivity of the metallacycles (2).



(1) R = H or $SiMe_3$



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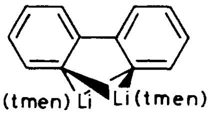

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Results and Discussion

The use of LiBu^n in conjunction with tertiary amines is an important method for direct metallation of organic substrates. By far the most common amine used is tmen (*NNN′N′*-tetramethylethylenediamine) and a ratio of 1 : 1 for LiBu^n to amine is found to be that with the greatest selectivity.[9] A more recently studied co-factor for LiBu^n is pmdien (pentamethyldiethylenetriamine) which for a 1 : 1 ratio maintains selectivity but there is an increase in reactivity.[10,11] Metallation in this paper has been restricted to using Li(tmen)Bu^n in hexane, primarily because pmdien-complexed lithium alkyls appear to be less versatile as alkyl transfer reagents. 2,2′-Dimethylbiphenyl, (6), was found to be dilithiated in high yield to afford a crystalline complex (7) which was derivatised as 2,2′-bis(trimethylsilylmethyl)biphenyl, (8) (Scheme 1). In contrast, for isomeric xylenes [12] and methylated naphthalenes [13] there is resistance to the formation of dilithiated species in synthetically viable quantities, attributed to a decrease in acidity of

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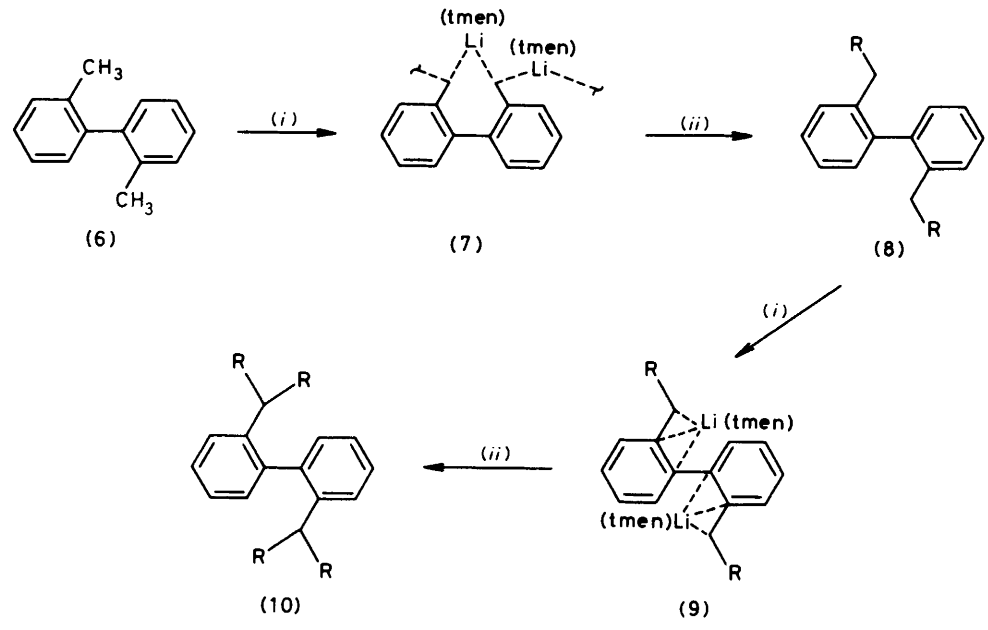
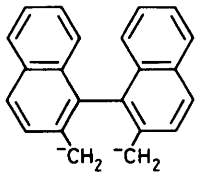
† α,α′-Bis[(*NNN′N′*-tetramethylethylenediamine)lithio]-2,2′-dimethylbiphenyl and -2,2′-bis(trimethylsilylmethyl)biphenyl.

Supplementary data available (No. SUP 23746, 30 pp.): structure factors, thermal parameters, least-squares planes, H-atom parameters. 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. R = SiMe$_3$. (*i*) 2 Li(tmen)Bu^n in hexane; (*ii*) 2 SiMe$_3$Cl, hexane



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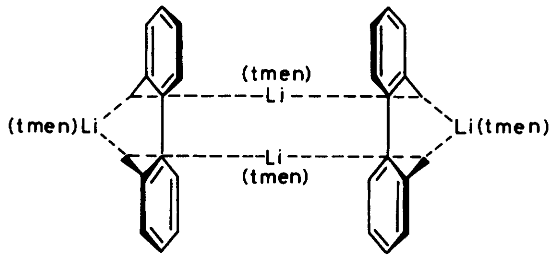


(5)

Table 1. Physical characteristics of the lithium-alkyl precursors and derivatives

Compd.^{a}	Analysis^b (%) C	H	B.p.^{c}/°C (0.1 mmHg)	Yield^d (%)
(8)	73.5 (73.55)	9.5 (9.25)	120	59
(10)	66.65 (66.3)	9.9 (9.85)	180—182	63
(12)	80.35 (80.25)	8.55 (8.7)	92—94	92
(13)	76.85 (77.6)	6.15 (6.05)	110—112	93
(15)	73.35 (73.55)	8.95 (9.25)	108—110	95

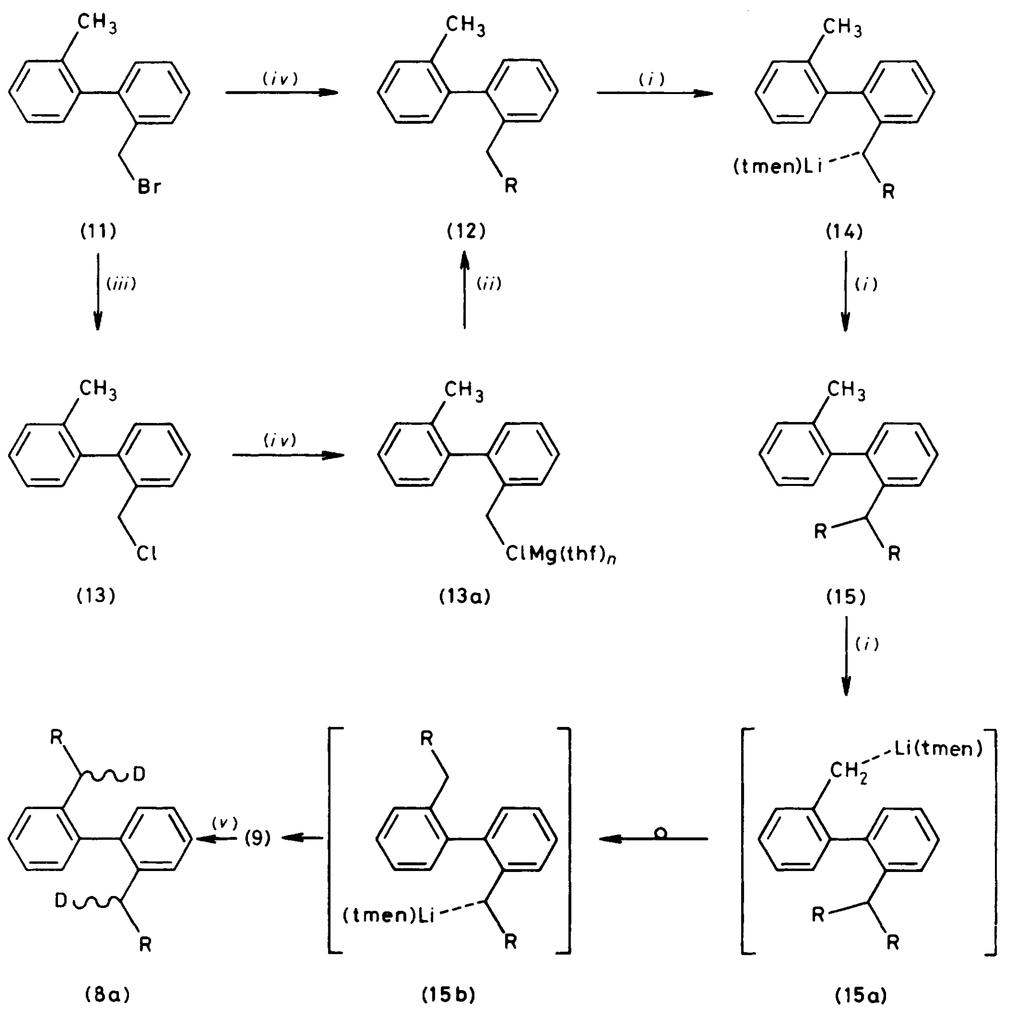
^{a} Colourless liquids; the lithium alkyls (7), (9), and (14) are orange-yellow. ^{b} Calculated values are given in parentheses. Analysis for (7): C, 73.2 (73.2); H, 10.25 (10.4). ^{c} For (7), (9), and (14) m.p.s are 102 (decomp.), 144—146, and 127—128 °C respectively (under an argon atmosphere in sealed capillaries). ^{d} Yields of (7), (9), (13a), and (14) are 94, 60, 60, and 85% respectively.

the benzylic protons as a consequence of delocalisation of charge to the aromatic ring(s)[10] and the electron-releasing properties of the residual methyl groups.[13] In the present study the dianion has only one charge associated with each potentially resonance-stabilising benzene ring and each segment of (6) behaves similarly to the lithiation of toluene which is likewise a high-yield reaction.[14] A related dianion is (4) (not isolated), prepared by the dilithiation of 2,2′-dimethyl-1,1′-binaphthyl and derivatised as a silicon heterocycle by condensation with SiMe$_2$Cl$_2$.[15] Metallation of (6) and (8) [and the formation of (4)] is in accordance with the following thermodynamic acidity inequalities:[10] $\mathrm{R{-}H < R{-}CH_3 \sim R{-}SiMe_3 < R{-}C\mathit{H}_2SiMe_3 < R{-}C\mathit{H}(SiMe_3)_2}$, R = aryl. Interestingly, metallation of unsubstituted biphenyl results in formation of a 2,2′-dilithio-species, (3).[16] Attempts selectively to monolithiate (6) using either tmen or pmdien co-factor were unsuccessful. Quenching the reaction mixtures with SiMe$_3$Cl in all cases afforded mixtures of (6), (8), and (12) in a typical ratio of 4 : 3 : 1 (gas-chromatographic mass spectrum results).

Lithiation and formation of derivatives of (8) is similar to that of (6), *viz.* dilithiation to produce a crystalline compound, (9), and the incorporation of two $^-$SiMe$_3$ groups on condensation with SiMe$_3$Cl (Scheme 1). Again no selective monolithiation was evident using one mol equiv. of Li(tmen)Bu^n. The crystalline product obtained was (9), although in low yield (33%). A compound related to (8), α,α′-bis(trimethylsilyl)-*o*-xylene, is also only dilithiated with one mol equiv. of Li(tmen)Bu^n,[10] in accordance with the above inequalities.

As expected the C$_\alpha$ protons of the $^-$CH(SiMe$_3$)$_2$ groups in (9) are inert, for the conditions and reagents used, a result of protective binding of the bulky $^-$SiMe$_3$ and the close proximity of the other $^-$CH(SiMe$_3$)$_2$ substituent.[10] The tertiary carbon proton in CH(SiMe$_3$)$_3$ is also resistant to reaction in Li(tmen)-Bu^n for the former reason.[17]

Lithiations of the monosilylated and asymmetric bis-



Scheme 2. R = $SiMe_3$. (*i*) Li(tmen)Bu^n in hexane; (*ii*) $SiMe_3Cl$, hexane; (*iii*) LiCl, dmf; (*iv*) Mg, thf [+ $SiMe_3Cl$ for (11) $\longrightarrow$ (12)]; (*v*) DCl–D_2O

silylated compounds, (12) and (15) respectively, are dissimilar to those of (6) and (8) since (12) is only monolithiated and (15) undergoes a 1,6-silyl migration to yield (9) as shown by formation of a silyl derivative, (10), and a dideuterio-species, (8a) (Scheme 2). The lack of dilithiation of (12) is surprising given the availability of (7) and (9). Furthermore, the ability to prepare (9) clearly demonstrates the origin of restricted metallation is not a steric effect; a conceivable cause comes from consideration of the *X*-ray structure results of (7) and (9) (see structural commentary). Metal–alkyl interactions in (7) are of the three-centre two-electron type, as found in bis(bicyclo[1.1.0]butan-1-yl)bis[(*NNN'N'*-tetramethylethylenediamine)lithium],[18] whereas (9) is best described as a 'contact ion-pair' type exemplified by the bonding in [{Li(tmen)}(CPh_3)].[19] In the structure of (9) extensive delocalisation of charge is assumed. The position of hydrogen abstraction of (12) is as predicted, at the carbon bearing the $SiMe_3$ group, and the mode of lithium–alkyl interaction in the derived complex is likely to belong to the category of a 'contact ion-pair' type accompanied by a delocalisation of charge. Such an effect may lower the acidity of the $^-CH_3$ group if charge delocalisation is extended to the second phenyl ring. (However, delocalisation is expected to be small in view of a possibly large dihedral angle between the two aromatic rings.) With $^-CH_2SiMe_3$ rather than $^-CH_3$ on the adjacent ring the anticipated increase in $^-CH_2SiMe_3$ acidity may effectively compensate this effect. In the case of (6) if the monolithio-species bonding is similar to that in (7) the nature of the lithium–alkyl interaction would allow little prospect for charge delocalisation and thus lowering of the acidity of the residual $^-CH_3$ group.

As to the novel 1,6-silyl migration, the proposed mechanism involved (outlined in Scheme 2) is $^-CH_3$ lithiation, to give (15a) [the most acidic, $^-CH(SiMe_3)_2$ is sterically inaccessible], followed by migration, to give (15b), and subsequent dilithiation to form (9), the same product as that of dilithiation of (8). The product is exclusively (9) even with one mol equiv. of Li(tmen)Bu^n, although in low yield (28%). This, plus the selective dilithiation of (8) with a one mol equiv. of Li(tmen)-Bu^n suggests the rate-determining step is either generation of (15a) or (15b). A similar migration has been noted in the lithiation of 9,10-dihydro-9,9-bis(trimethylsilyl)anthracene, but using LiBu^n in tetrahydrofuran (thf), where $H_2C(10)$ metallation is followed by a 1 $\longrightarrow$ 4 silyl migration and the product is not further lithiated.[20] This and other anionic silyl migrations [21] are thought to arise *via* the silyl entity shifting intramolecularly through a five-co-ordinate intermediate.[22]

In thf (7) is monomeric and in benzene it is dimeric (Signer method), thus indicating an electron precise compound in thf with a thf molecule attached to each lithium as found in [$(CH_2)_3S_2C(Ph)Li(tmen)(thf)$],[23] and the retaining of the solid-state type bonding in benzene. Molecular model considerations,

Table 2. Hydrogen-1 n.m.r. data [a,b] for selected compounds

Compd.	R–CH_3	R–CH_2	R–CH	$Si(CH_3)_3$	$(C_6H_4)_2$	N–CH_3	N–CH_2
(7) [c]		8.74 (s) 4 H			3.70 (m) 6 H 4.52 (m) 2 H	8.65 (s) 24 H	8.70 (s) 8 H
(8)		8.08 (s) 4 H		10.58 (s) 18 H	2.96 (m) 8 H		
(9) [c]			*d*	10.11 (s) 18 H	4.53 (m) 2 H 3.57 (m) 6 H	8.85 (s) 24 H	8.92 (s) 8 H
(8a)			7.82 (s) 2 H	10.22 (s) 18 H	3.00 (m) 8 H		
(10)			8.23 (s) 2 H	9.92 (s) 18 H 10.03 (s) 18 H	3.00 (m) 8 H		
(12)	7.92 (s) 3 H	8.04 (s) 2 H		10.11 (s) 9 H	2.87 (m) 8 H		
(14) [c]	8.07 (s) 3 H		9.16 (s) 1 H	10.22 (s) 9 H	4.29 (m) 1 H 3.57 (m) 7 H	8.91 (s) 12 H	8.96 (s) 4 H
(13)	7.95 (s) 3 H	5.67 (s) 2 H			2.76 (m) 8 H		
(15)	8.03 (s) 3 H		8.43 (s) 1 H	10.10 (s) 9 H 10.18 (s) 9 H	2.86 (m) 8 H		

[a] Values quoted in τ relative to external $SiMe_4$ (τ 10). In $CDCl_3$ unless otherwise stated. [b] R = Aryl. [c] In C_6D_6. [d] Not observed.

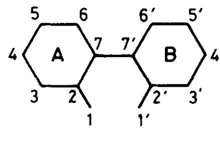
optimizing *X*-ray structural details, suggest (5) to be the most plausible structure of the dimer. The existence of an oligomer (electron deficient) in solution is further evidence that 'contact ion-pair' bonding (electron precise) is not a salient feature of bonding. For a series of α-trimethylsilyl-*o*-xylenes, monomeric the 'contact ion-pair' compounds in the solid behave as monomers in non-co-ordinating solvents.[24] Therefore it is not unreasonable to predict that related compounds (9) and (12) are also monomeric in solution. This is supported by the structure of (9) being monomeric and essentially a 'contact ion-pair' type.

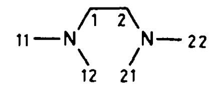
Analytical data and physical characteristics of all new compounds are presented in Table 1. Proton and ^{13}C n.m.r. data are in Tables 2 and 3, respectively.

Protons *para* to $^-$CHR (R = H or $SiMe_3$) exhibit ^1H n.m.r. resonances upfield by τ 0.7—1.0, relative to other protons of the same phenyl group, and also to those of the adjacent ring (Table 2). This phenomenon is similar to the analogous *para* protons of lithio-*o*-xylene species.[12] No $^{13}C-^7Li$ coupling was detected for (7), (9), and (14), a common occurrence for organolithium compounds, which has been attributed to a combination of bond exchange, likely in the 'contact ion-pair' structures (9) and (12), and ^7Li quadrupole relaxation.[25] Other n.m.r. data are unexceptional, being similar to those of *o*-xylene and α-trimethylsilylated *o*-xylene lithium alkyls.[10]

Compound (12) has been prepared by two routes, a Grignard *in situ* reaction involving $SiMe_3Cl$ and 2-bromomethyl-2′-methylbiphenyl, (11), and by quenching with $SiMe_3Cl$ the Grignard reagent of the analogous chloride, (13) prepared from (11) *via* its reaction with LiCl in dimethylformamide (dmf). The Grignard reagent was prepared in modest yields (60%), whereas attempted synthesis using the bromo-compound (11) typically gave a low yield (20%). The use of chloride rather than bromide to limit the competing coupling reactions is well known even for simple Grignard reagents [26] and for benzylic Grignards is highlighted by the critical conditions of concentration, temperature, and solvent required for high-yield di-Grignard reagents of α,α′-dichloro-*o*-xylene [2] and 2,2′-bis(chloromethyl)biphenyl.[5]

Structural Commentary.—Compound (7). The structure determination confirms the assignment of stoicheiometry as $[\{Li(tmen)\}_2\{(2-CH_2C_6H_4)_2\}]$; one formula unit comprises the asymmetric unit of the structure, the nature of which is an infinite polymer generated by the 4_1 screw axis of the space group along *c* (Figure 1). The atom numbering for the non-hydrogen atoms is as shown; hydrogen atom numbering following that of the parent atom with suffixes a,b,c.





Within the biphenyl anion, the two crystallographically independent rings are twisted relative to each other about the bond between them, the dihedral angle being 73.7°; the two methylene groups, C(1A) and C(1B), are bridged by one of the lithium atoms [Li(B)] at distances of 2.28(3) and 2.16(3) Å, the lithium atom being four-co-ordinate by virtue of its bonding to the associated tmen ligand [Li–N 2.21(3) and 2.10(3) Å]. The lithium atom lies 2.08 and 2.00 Å out of the A and B aromatic ring planes. The other lithium atom, Li(A), also bridges A and B, but from different dianions, related by the 4_1 screw; the lithium–methylene carbon distances are 2.28(3) and 2.46(3) Å respectively, with the lithium–tmen nitrogen distances [2.18(3) and 2.14(3) Å] making up the four-co-ordination about the lithium atom. The lithium atom lies 2.25 and 2.34 Å out of the A and B planes, respectively, on the opposite sides of the planes to their associated Li(B) atom. The angles subtended at the lithium atoms A and B by the tmen chelating ligands are 86.5(10) and 83.8(10)°, respectively, while the angles subtended at the methylene carbon atoms A and B are 162.6(11) and 157.5(11)° respectively. Taking into account the bond to the ring junctions from each methylene, the angles subtended at methylene carbons A and B by their Li_2C 'co-ordination spheres' sum to 358.9 and 360.0° respectively. It is further of interest that the methylene carbon–aromatic carbon distances are 1.44(2) and 1.42(2) Å for sections A and B respectively. Regrettably, the imprecision of the structure determination does not permit the experimental location of the associated hydrogen atoms; by implication from the above, the co-ordination about each methylene carbon may be trigonal bipyramidal. In compound (7), the lithium atoms are associated quite distinctly with the methylene carbon only; all other lithium–carbon distances are >2.8 Å.

Compound (9). The structure determination establishes the complex to have the stoicheiometry and structure $[\{Li(tmen)\}_2\{[2-CH(SiMe_3)C_6H_4]_2\}]$ (Figure 2); discrete species of this stoicheiometry are observed rather than the polymeric array of (7). The dihedral angle between the two aromatic C_6 planes is less than that in (7), being 54.3°; the deviations of the silicon atoms (A and B) from aromatic planes A and B respectively are 0.17 and 0.20 Å respectively. As usual in the structures of derivatives of this type, the $SiMe_3$ methyl substituents are disposed with two methyl groups astride

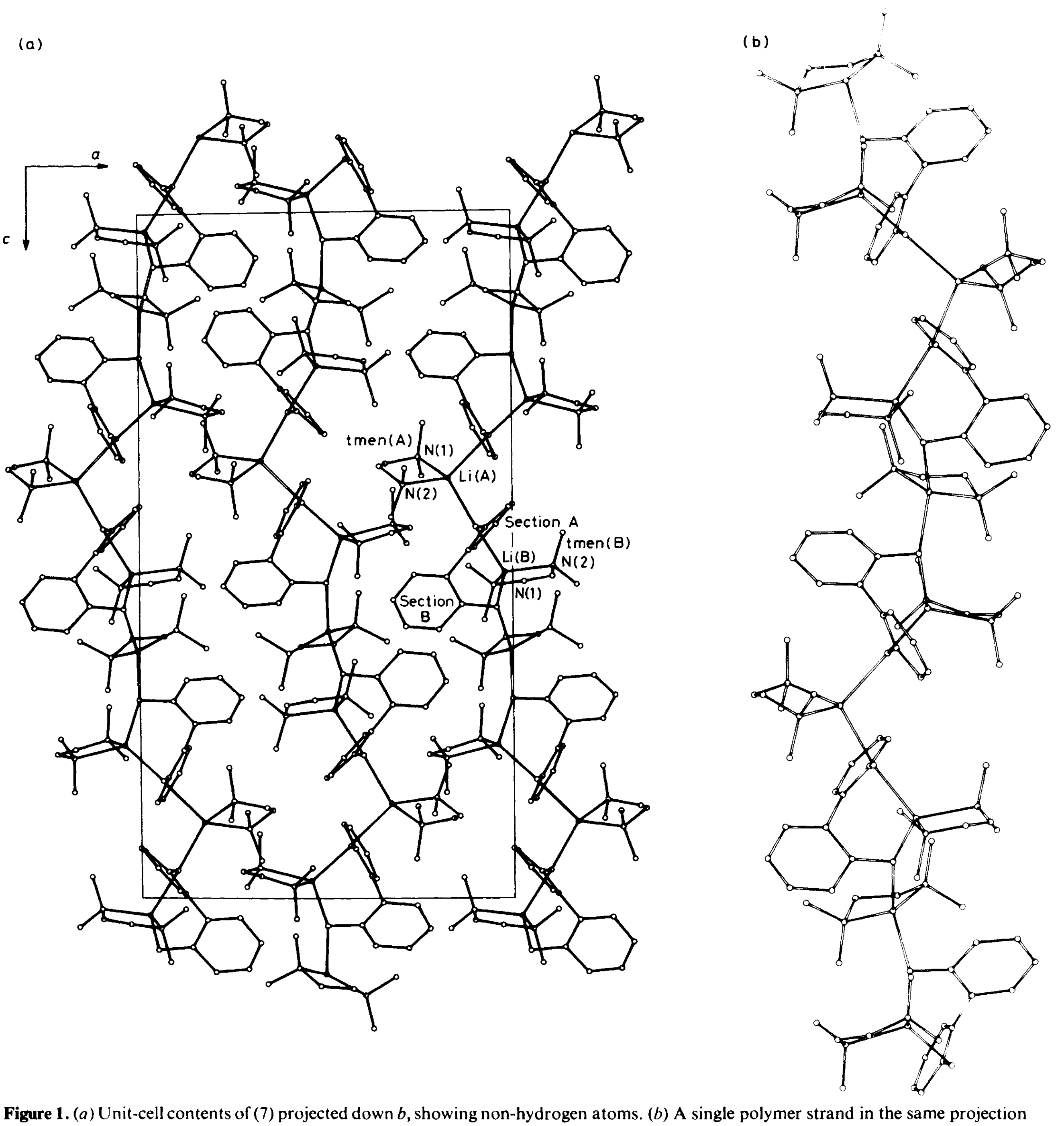


Figure 1. (*a*) Unit-cell contents of (7) projected down *b*, showing non-hydrogen atoms. (*b*) A single polymer strand in the same projection

H(3), so that the third is approximately coplanar with the aromatic plane [deviations of C(8A,B,C) in the present case are −0.32, −1.78, and 1.18 Å respectively (plane A); 1.75, 0.41, and −1.20 Å (plane B)]. The Li–C(1) distances [2.22(1) (A) and 2.19(2) Å (B)] are comparable to those observed in (7), as are the lithium–nitrogen distances in the tmen chelate rings although the latter [2.04(2)—2.10(1) Å] may be somewhat shorter. In this case, however, since polymer formation is presumably precluded by the presence of the bulky trimethylsilyl groups, the lithium atom may be reasonably considered to interact with more than the methylene carbon atom of the ligand; the distances from the lithium to C(2,7) are [2.33(1), 2.48(1) Å] (A) and [2.42(2), 2.63(1) Å] (B). The methylene carbon–aromatic ring distances are again short (this time with the benefit of improved precision), being 1.42(1) and 1.42(1) Å; although the interaction with the lithium gives the immediate impression of being of the 'contact ion-pair' type, {*cf.* $[\{Li(tmen)\}_2\{o\text{-}(Me_3SiCH)_2\text{-}C_6H_4\}]$ [10]}, the deviations of the silicon atom from the ring plane also suggest a non-negligible covalency may be present (*cf.* $[\{Li(pmdien)\}\{o\text{-}(Me_3SiCH)C_6H_4Me\}]$ [24]).

Experimental

General Procedures.—Owing to the air-sensitivity of all complexes, $SiMe_3Cl$, and the Grignard solution, (13a),

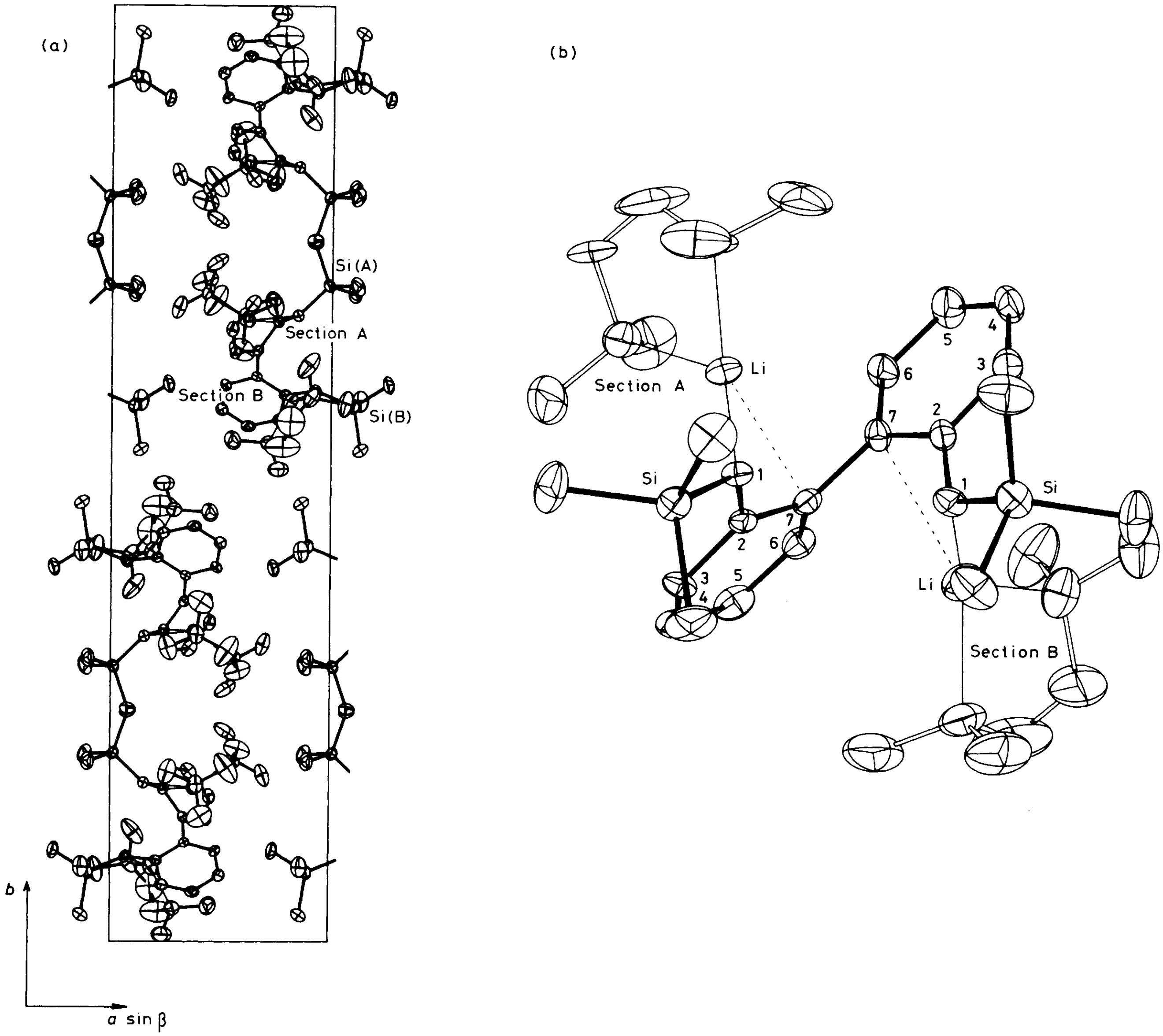


Figure 2. (*a*) Unit-cell contents of (9) projected down *c*; non-hydrogen atoms are shown with 20% thermal ellipsoids. (*b*) A single molecule of (9) projected down the pseudo-two-fold axis of the ligand

manipulations 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 $LiAlH_4$ (pentane and thf), KOH (tmen), and CaH_2 (hexane).

Physical and Analytical Measurements.—Elemental analyses were performed by the Australian Mineral Development Laboratories, Melbourne. 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., ^{13}C n.m.r., and mass spectra were recorded on Hitachi-Perkin-Elmer R-24B (60 MHz), Brüker WP-80, and Brüker HP-5986 spectrometers respectively. The molecular weight of compound (7) was determined using the Signer method.

Syntheses of the lithium alkyls are similar and consequently only that of one of them, (8), is detailed below.

Synthesis of $[\{Li(tmen)\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$ (7).—2,2′-Dimethylbiphenyl was prepared from *o*-iodotoluene by the method of Hall *et al.*[27] To a cooled (0 °C) solution of $LiBu^n$ in hexane (20 cm^3, 1.7 mol dm^{-3}, 34 mmol) was added tmen (5.4 cm^3, 35 mmol) dropwise with stirring, followed by (6) (3.15 g, 17 mmol) and the clear solution left for 12 h at room temperature. An orange-yellow precipitate was then collected, washed with pentane (3 × *ca.* 5 cm^3) and dried *in vacuo* (6.9 g, 94%), m.p. 102 °C (decomp.). Molecular weight (30 °C): found 490 (thf), 927 (benzene); calculated 426.3 (monomer).

Synthesis of 2,2′-*Bis*(*trimethylsilylmethyl*)*biphenyl*, (8).—To a stirred suspension of (7) (6.4 g, 15 mmol) in hexane (20 cm^3) at 0 °C was slowly added $SiMe_3Cl$ (3.6 g, 33 mmol). After stirring for 1 h at room temperature, excess $SiMe_3Cl$ and thf were removed *in vacuo* and dilute HCl added (20 cm^3, 2 mol dm^{-3}). The product was then extracted with hexane (30 cm^3) and distilled (3.1 g, 59%), b.p. 120 °C (0.1 mmHg). Mass spectrum, *m*/*e* 326 (P^+), 253; i.r., 3 070w, 3 030w, 2 983m, 2 905w, 1 600w, 1 578w, 1 499w, 1 481m, 1 447w, 1 251s, 1 200m, 1 160m, 1 072w, 1 053w, 1 009w, 947w, 848s, 768m, 750m, 750s, and 690w cm^{-1}.

Table 3. Carbon-13 n.m.r. data [a,b] for compounds (7)—(10) and (12)—(15)

Compound	R–CH$_3$	R–CH$_2$	R–CH	Si(CH$_3$)$_3$	(C$_6$H$_4$)$_2$	N–CH$_2$	N–CH$_3$
(7) [c]		36.8			154.4, 129.1, 127.7, 126.5, 117.7, 106.4	57.6	46.2
(8)		23.9		−0.8	140.8, 138.9, 131.4, 129.0, 127.2, 124.3		
(9) [c]			50.5	3.1	153.1, 132.1, 129.8, 127.3, 121.2, 107.2	56.9	45.6
(10)			24.1	2.4 1.7	142.1, 140.8, 134.0, 129.5, 126.9, 122.7		
(12)		23.6		0.9	142.0, 140.3, 138.7, 136.1, 130.5, 130.0, 129.5, 129.1, 127.3, 127.1, 125.6, 124.2		
(14) [c]	20.6		39.7	2.9	131.6, 131.0, 129.7, 127.3, 126.6, 126.3, 120.1, 110.1	56.5	45.0
(13)	20.1	44.0			139.5, 136.0, 135.4, 130.1, 129.9, 129.5, 128.2, 127.9, 127.2, 125.6		
(15)	20.8		23.9	1.1	141.5, 140.1, 136.2, 131.1, 130.6, 129.2, 127.2, 127.0, 125.1, 123.2		

[a] Values in p.p.m. relative to SiMe$_4$ (0 p.p.m.) calculated from the shifts for C$_6$D$_6$ (128.0 p.p.m.) and CDCl$_3$ (77.0 p.p.m.). [b] R = Aryl. [c] In C$_6$D$_6$.

Table 4. Non-hydrogen atom co-ordinates for (7)

	Section A			Section B		
Atom	x	y	z	x	y	z
Li	0.828 4(15)	0.505 8(17)	0.388 4(8)	0.978 9(15)	0.542 4(14)	0.525 8(8)
Dianion ligand						
C(1)	0.902 1(9)	0.501 7(10)	0.459 5(4)	0.956 7(10)	0.438 5(9)	0.577 1(4)
C(2)	0.926 5(11)	0.409 7(10)	0.460 9(5)	0.864 0(11)	0.424 7(9)	0.572 6(5)
C(3)	0.989 7(11)	0.374 0(12)	0.430 6(5)	0.802 0(14)	0.455 8(10)	0.608 9(5)
C(4)	1.000 5(12)	0.284 2(15)	0.426 8(6)	0.713 3(15)	0.440 6(13)	0.604 4(8)
C(5)	0.955 8(15)	0.226 7(11)	0.455 7(6)	0.680 4(11)	0.396 0(13)	0.565 7(9)
C(6)	0.897 9(11)	0.260 6(13)	0.489 5(5)	0.736 1(12)	0.369 3(10)	0.529 0(6)
C(7)	0.882 2(10)	0.352 3(10)	0.493 7(6)	0.823 8(11)	0.382 3(9)	0.532 4(6)
tmen ligands						
C(1)	0.660 6(14)	0.432 9(15)	0.366 8(10)	1.031 0(21)	0.726 3(13)	0.539 5(9)
N(1)	0.748 2(9)	0.400 9(8)	0.357 5(5)	0.949 4(11)	0.680 9(8)	0.545 0(5)
C(11)	0.757 4(13)	0.320 0(12)	0.384 6(6)	0.882 3(15)	0.717 1(13)	0.516 7(8)
C(12)	0.761 5(12)	0.379 9(13)	0.307 9(5)	1.171 4(11)	0.540 2(13)	0.544 5(6)
C(2)	0.644 4(11)	0.520 2(16)	0.370 6(7)	1.106 2(18)	0.677 0(18)	0.532 4(15)
N(2)	0.707 3(8)	0.577 5(9)	0.397 3(4)	1.108 7(8)	0.589 8(10)	0.517 5(5)
C(21)	0.675 6(11)	0.587 9(13)	0.444 6(6)	0.924 0(13)	0.680 9(13)	0.594 9(7)
C(22)	0.712 4(11)	0.662 6(12)	0.373 7(7)	1.135 2(12)	0.584 4(19)	0.469 5(7)

Synthesis of [{Li(tmen)}$_2${[2-CH(SiMe$_3$)C$_6$H$_4$]$_2$}] (9).—The same procedure as for (7) was used [LiBu^n (4 cm^3, 1.7 mol dm^{-3}, 7 mmol); tmen (1.3 cm^3, 8.6 mmol); (8) (1.0 g, 3 mmol)]; yield 1.0 g, 60%; m.p. 144—146 °C.

Synthesis of [2-(Me$_3$Si)$_2$CHC$_6$H$_4$]$_2$ (10).—The same procedure as for (8) was used [(9) (3.16 g, 5.5 mmol); hexane (10 cm^3); SiMe$_3$Cl (4 cm^3, 30 mmol)], yield on distillation 1.8 g (63%), b.p. 180—182 °C (0.1 mmHg), except the distillate on standing afforded white crystals, m.p. 63—64 °C. Mass spectrum, *m/e* 470 (P^+), 367, 279; i.r., 3 070w, 2 965s, 2 915w, 1 600w, 1 472w, 1 438m, 1 255s, 1 190m, 1 110w, 1 030w, 1 010w, 950w, 850s, 755m, 770s, 684m, and 612w cm^{-1}.

Synthesis of 2-Methyl-2′-(trimethylsilylmethyl)biphenyl, (12).—2-(Bromomethyl)-2′-methylbiphenyl, (11), was prepared by the method of Wittig *et al.*[28] To a stirred suspension of magnesium powder (1.7 g, 70 mmol) in thf (20 cm^3), preactivated with BrCH$_2$CH$_2$Br, and SiMe$_3$Cl (1.3 cm^3, 10 mmol) was slowly added a solution of (11) (14 g, 50 mmol) in thf (50 cm^3) over 2 h. After stirring at room temperature for a further 2 h, excess SiMe$_3$Cl and thf were removed *in vacuo*, and HCl added (2 mol dm^{-3}, 20 cm^3). The product was extracted with hexane (100 cm^3) and distilled (7.5 g, 55%), b.p. 92—94 °C (0.1 mmHg). Mass spectrum, *m/e* 254 (P^+), 239, 165; i.r., 3 075w, 3 032w, 2 965m, 1 604w, 1 482m, 1 450w, 1 385w, 1 250s, 1 200m, 1 167m, 1 120w, 1 010w, 945w, 850s, 751s, and 690w cm^{-1}.

Table 5. Non-hydrogen atom co-ordinates for (9)

	Section A			Section B		
Atom	x	y	z	x	y	z
Li	0.623 9(10)	0.666 3(3)	−0.124 8(10)	0.812 5(13)	0.579 9(3)	0.240 9(1)
Dianion ligand						
Si	0.986 7(2)	0.703 40(5)	0.104 0(2)	1.102 2(2)	0.575 13(6)	0.141 1(2)
C(81)	1.115 5(7)	0.703 1(2)	0.229 76(7)	1.132 0(8)	0.580 6(2)	−0.017 3(8)
C(82)	0.919 9(8)	0.748 3(2)	0.059 6(8)	1.258 1(7)	0.598 7(2)	0.286 2(7)
C(83)	1.104 8(7)	0.694 7(2)	0.017 5(8)	1.132 7(8)	0.528 7(2)	0.186 2(8)
C(1)	0.847 1(6)	0.671 1(2)	0.053 7(5)	0.931 5(6)	0.592 1(2)	0.122 6(6)
C(2)	0.755 7(6)	0.664 1(2)	0.117 3(6)	0.788 7(7)	0.587 7(2)	0.009 3(7)
C(3)	0.740 2(7)	0.688 2(2)	0.209 4(7)	0.761 3(7)	0.561 4(2)	−0.091 2(8)
C(4)	0.641 2(10)	0.684 6(2)	0.259 6(7)	0.623 3(9)	0.553 8(2)	−0.196 3(8)
C(5)	0.548 6(8)	0.656 9(2)	0.225 3(8)	0.501 8(8)	0.571 2(2)	−0.209 9(8)
C(6)	0.562 7(7)	0.632 2(2)	0.141 4(7)	0.521 1(7)	0.597 5(2)	−0.117 1(8)
C(7)	0.664 7(7)	0.634 3(2)	0.088 3(6)	0.660 0(7)	0.606 9(1)	−0.008 6(6)
tmen ligands						
C(1)	0.413 8(12)	0.705 8(3)	−0.336 2(10)	0.819 4(23)	0.560 4(6)	0.489 2(17)
N(1)	0.437 9(7)	0.696 4(2)	−0.196 9(7)	0.910 5(9)	0.583 8(3)	0.459 4(7)
C(11)	0.308 5(10)	0.681 0(3)	−0.198 1(10)	1.065 8(11)	0.578 8(3)	0.527 9(9)
C(12)	0.471 2(11)	0.726 8(3)	−0.110 6(9)	0.892 2(15)	0.617 4(4)	0.501 4(10)
C(2)	0.486 3(15)	0.689 0(4)	−0.390 6(11)	0.767 8(27)	0.532 3(4)	0.405 9(17)
N(2)	0.608 0(8)	0.669 3(20)	−0.321 7(6)	0.712 8(8)	0.536 7(2)	0.258 5(10)
C(21)	0.735 8(11)	0.683 8(3)	−0.321 3(8)	0.553 0(11)	0.538 1(2)	0.178 9(12)
C(22)	0.585 7(12)	0.636 0(3)	−0.387 0(9)	0.760 5(11)	0.508 7(3)	0.201 0(12)

Table 6. Non-hydrogen atom geometry for (7) (distances in Å, angles in °); the two values in each entry are for sections A, B

Dianion ligand					
Li–C(1)	2.28(3), 2.16(3)	Li–C(1)–C(2)	100(1), 102(1)	C(4)–C(5)–C(6)	119(2), 121(2)
C(1)–C(2)	1.44(2), 1.42(2)	C(1)–C(2)–C(3)	122(1), 121(1)	C(5)–C(6)–C(7)	122(2), 120(2)
C(2)–C(3)	1.39(2), 1.46(2)	C(1)–C(2)–C(3)	119(1), 124(1)	C(6)–C(7)–C(2)	117(1), 123(1)
C(2)–C(7)	1.43(2), 1.43(2)	C(3)–C(2)–C(7)	119(1), 115(1)	C(6)–C(7)–C(7)	118(1), 120(1)
C(3)–C(4)	1.37(3), 1.37(3)	C(2)–C(3)–C(4)	121(2). 121(2)	C(2)–C(7)–C(7)	125(1) 118(1)
C(4)–C(5)	1.37(3), 1.37(3)	C(3)–C(4)–C(5)	122(2), 121(2)		
C(5)–C(6)	1.39(3), 1.39(3)				
C(6)–C(7)	1.41(2), 1.34(2)				
C(7)–C(7)	1.47(2)				
tmen ligands					
Li–N(1)	2.18(3), 2.21(3)	Li–N(1)–C(1)	101(1), 105(1)	Li–N(2)–C(21)	117(1), 112(1)
Li–N(2)	2.14(3), 2.10(3)	Li–N(1)–C(11)	111(1), 112(1)	Li–N(2)–C(22)	110(1), 111(1)
N(1)–C(1)	1.43(3), 1.42(3)	Li–N(1)–C(12)	118(1), 107(1)	C(2)–N(2)–C(21)	109(1), 111(2)
N(2)–C(2)	1.49(2), 1.38(3)	C(1)–N(1)–C(11)	106(1), 112(2)	C(2)–N(2)–C(22)	109(1), 111(2)
C(1)–C(2)	1.35(3), 1.37(4)	C(1)–N(1)–C(12)	112(2), 110(2)	C(21)–N(2)–C(22)	110(1), 107(1)
N(1)–C(11)	1.45(2), 1.40(3)	C(11)–N(1)–C(12)	108(1), 111(2)	N(1)–C(1)–C(2)	121(2), 118(2)
N(1)–C(12)	1.44(2), 1.46(2)	Li–N(2)–C(2)	101(1), 105(1)	N(2)–C(2)–C(1)	120(2), 126(2)
N(2)–C(21)	1.42(2), 1.43(2)				
N(2)–C(22)	1.45(2), 1.41(2)				
Li(B)–C(A1)	2.28(3)	Li(B)–C(A1)–Li(A)	163(1)	Li(B)–C(A1)–C(2)	96(1)
Li(A)–C(B1)	2.46(3)	C(A1)–Li(B)–C(B1)	106(1)		

Synthesis of 2-Chloromethyl-2′-methylbiphenyl, (13).—Lithium chloride (1.5 g, 40 mmol) was added to a mixture of dmf (40 cm^3) and (11) (3.0 g, 10 mmol), stirred for 2 h, and then added to hexane (30 cm^3) and water (20 cm^3). Concentration of the hexane portion and distillation yielded a pale yellow liquid (2.2 g, 93%), b.p. 110—112 °C (0.1 mmHg). Mass spectrum, *m/e* 218, 216 (P^+), 181, 180, 179, 166, 165; i.r., 2 980br, 2 865m, 2 034w, 1 468m, 1 382m, 1 265m, 1 110br, 940m, 800w, 785w, and 622s cm^{-1}.

Preparation of the Grignard Reagent (13a).—To a suspension of activated magnesium powder (0.15 g, 6 mmol) in thf (5 cm^3) was added dropwise a solution of (13) (0.66 g, 3 mmol) in thf (30 cm^3) over a period of 2 h during which the solution became pale green. Stirring was continued for a further 2 h at room temperature whereupon the solution was filtered into a calibrated flask. Standardisation *via* quenching 1-cm^3 aliquots with 0.1 mol dm^{-3} HCl and titrating with 0.1 mol dm^{-3} NaOH indicated the Grignard was formed in 60% yield (concentration 0.087 mol dm^{-3}).

Preparation of (12) *from* (13a).—To the above solution of (13a) at 0 °C, SiMe$_3$Cl (0.8 cm^3, 6 mmol) was added dropwise in thf (10 cm^3) over 10 min. The solution was then stirred for

Table 7. Non-hydrogen geometry for (9) (distances in Å, angles in °); the two values in each entry are for sections A, B

Dianion ligand geometry					
C(1)–C(2)	1.42(1), 1.42(1)	Si–C(1)–C(2)	127.0(5), 128.0(5)	C(3)–C(2)–C(7)	114.7(7), 115.2(5)
Si–C(81)	1.889(6), 1.883(10)	C(1)–Si–C(81)	112.5(3), 114.6(3)	C(2)–C(3)–C(4)	123.4(7), 123.3(7)
Si–C(82)	1.875(7), 1.886(6)	C(1)–Si–C(82)	116.1(3), 108.7(3)	C(3)–C(4)–C(5)	121.7(8), 121.3(7)
Si–C(83)	1.873(10), 1.875(8)	C(1)–Si–C(83)	109.2(3), 115.2(4)	C(4)–C(5)–C(6)	117.5(9), 118.3(6)
C(2)–C(3)	1.43(1), 1.43(1)	C(81)–Si–C(82)	106.0(3), 105.5(4)	C(5)–C(6)–C(7)	123.3(7), 123.0(7)
C(2)–C(7)	1.44(1), 1.45(1)	C(81)–Si–C(83)	105.5(3), 105.6(4)	C(2)–C(7)–C(6)	119.2(6), 118.8(6)
C(3)–C(4)	1.36(1), 1.38(1)	C(82)–Si–C(83)	106.8(4), 106.6(3)	C(2)–C(7)–C(7)	123.3(7), 123.4(5)
C(4)–C(5)	1.38(1), 1.37(1)	C(1)–C(2)–C(3)	121.1(6), 120.4(6)	C(6)–C(7)–C(7)	117.1(6), 117.6(6)
C(5)–C(6)	1.38(1), 1.39(1)	C(1)–C(2)–C(7)	124.0(6), 124.3(6)		
C(6)–C(7)	1.41(1), 1.41(1)				
C(7)–C(7′)	1.49(1)				
Si–C(1)	1.799(6), 1.797(7)				
Li–C(1)	2.22(1), 2.19(2)				
Li–C(2)	2.33(1), 2.42(2)				
tmen ligands					
Li–N(1)	2.07(1) 2.10(1),	Li–N(1)–C(1)	102.7(7), 100.4(8)	Li–N(2)–C(21)	112.6(5), 113.0(7)
Li–N(2)	2.06(1) 2.04(2),	Li–N(1)–C(11)	116.5(6), 114.4(8)	Li–N(2)–C(22)	111.8(7), 107.9(9)
N(1)–C(1)	1.45(1), 1.45(3)	Li–N(1)–C(12)	109.0(5), 110.9(7)	C(2)–N(2)–C(21)	112.5(10), 114.7(15)
N(2)–C(2)	1.36(1), 1.43(2)	C(1)–N(1)–C(11)	112.3(7), 118.6(11)	C(2)–N(2)–C(22)	110.3(8), 110.2(10)
C(1)–C(2)	1.32(2), 1.37(3)	C(1)–N(1)–C(12)	109.3(7), 108.7(13)	C(21)–N(2)–C(22)	107.5(9), 106.6(7)
N(1)–C(11)	1.45(1), 1.43(1)	C(11)–N(1)–C(12)	106.9(8), 103.8(9)	N(1)–C(1)–C(2)	118.1(9), 117.3(20)
N(1)–C(12)	1.45(1), 1.44(2)	Li–N(2)–C(2)	102.2(8), 104.3(10)	N(2)–C(2)–C(1)	127.3(10), 118.0(15)
N(2)–C(21)	1.43(1), 1.46(1)				
N(2)–C(22)	1.45(1), 1.46(2)				

1 h at room temperature. The remaining procedure was as for the synthesis of (12) from (11) (0.47 g, 92%), b.p. 92—94 °C (0.1 mmHg).

Monolithiation of (12).—Attempted dilithiation of (12) in the same manner as the syntheses of (7) and (9) [LiBu^n (14.5 cm^3, 25 mmol); tmen (3.8 cm^3, 25 mmol); (12) (3.0 g, 12 mmol)] resulted in a monolithiated product, (14) (3.17 g, 85%), m.p. 127—128 °C.

Synthesis of 2-[*Bis*(*trimethylsilyl*)*methyl*]-2′-*methylbiphenyl*, (15).—Identical conditions were used as for the syntheses of (8) and (10) [(14) (3.7 g, 10 mmol); hexane (10 cm^3); SiMe$_3$Cl (2.5 cm^3, 20 mmol)], yield on distillation 3.1 g (95%), b.p. 108—110 °C (0.1 mmHg). Mass spectrum, *m*/*e* (P^+) 326, 238, 223; i.r., 3 070m, 3 030m, 2 960s, 1 955w, 1 925w, 1 600m, 1 500m, 1 478s, 1 440m, 1 383w, 1 251s, 1 193m, 1 042m, 1 010m, 945w, 855s, 770s, 750s, 730m, 684m, 655w, and 614m cm^{-1}.

Attempted Monolithiation of (15).—To a solution containing LiBu^n (0.5 cm^3, 1.7 mol dm^{-3}, 0.86 mmol) and tmen (0.12 cm^3, 0.86 mmol) at 0 °C was added (15) (0.25 g, 0.8 mmol) and the mixture left for 12 h at room temperature. The resulting yellow-orange crystals were washed with pentane (3 × 5 cm^3) yielding 0.13 g (30%) of (9). These were dissolved in hexane (10 cm^3), and the solution was cooled to 0 °C whereupon DCl [0.5 cm^3, 5 mol dm^{-3} (D$_2$O), 2.5 mmol] was added dropwise. Extraction with hexane (10 cm^3) and concentration yielded exclusively the dideuterio-species, (8a), as shown by ^{1}H n.m.r. (Table 2) and a gas-chromatographic mass spectrum. Using 2 mol equiv. of Li(tmen)Bu^n a higher yield of (9) (60%) was obtained.

Crystallography.—*Crystal data for* (7). $C_{26}H_{28}Li_2N_4$, M = 410.0, Tetragonal, space group $P4_12_12$ ($D_4{}^4$, no. 92), a = 15.11(1), c = 28.11(2) Å, U = 6 421(7) Å^3, Z = 8, D_c = 0.85 g cm^{-3}, F(000) = 1 744. Monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ_{Mo} = 0.54 cm^{-1}. Specimen: irregular, *ca.* 0.2 mm, enclosed in capillary.

Crystal data for (9). $C_{32}H_{60}Li_2N_4Si_2$, M = 570.8, Monoclinic, space group $P2_1/c$ ($C_{2h}{}^5$, no. 14), a = 10.265(4), b = 39.297(12), c = 10.801(5) Å, β = 117.52(3)°, U = 3 864(3) Å^3, Z = 4, D_c = 0.98 g cm^{-3}, F(000) = 1 256, μ_{Mo} = 1.2 cm^{-1}. Specimen: irregular, *ca.* 0.3 mm, enclosed in capillary.

Structure determination. Unique data sets were measured within the limit $2\theta_{max.}$ = 45° at 295 K using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode; 2 480, for (7), and 5 070, for (9), independent reflections were obtained. Of these, 1 043, for (7), and 2 789, for (9), with $I > 3\sigma(I)$ were considered ' observed ' and used in the least-squares refinements without absorption correction after solution of the structures by direct methods. A 9 × 9 block-diagonal least squares was used, anisotropic thermal parameters being refined for the non-hydrogen atoms. Hydrogen atoms (x,y,z,U) were estimated, U being set at 1.25 $\bar{U}_{ii}$ (parent atom). Residuals (R,R') at convergence were 0.092 and 0.089 for (7), 0.066 and 0.051 for (2), reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$; the rather high residuals are attributed to the rapid fall-off in data density as a function of 2θ, high thermal motion and high hydrogen atom content. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[29] Computation used the *X*-RAY 76 program system [30] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

In the case of (7), thermal motion on the tmen methylene bridges was very high and probably indicates disorder, although the atoms were not resolved into independent components in difference maps. A few reflections close to the long axis were suppressed in refinement on account of profile overlap.

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References

1 J. P. Collman and L. S. Hegedus, ' Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California, 1980, p. 506.

2 M. F. Lappert, T. R. Martin, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 1959.

3 M. F. Lappert, T. R. Martin, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1980, 476.

4 M. F. Lappert, C. L. Raston, G. L. Rowbottom, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1981, 6; M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *ibid.*, 1981, 485.

5 W-P. Leung and C. L. Raston, *J. Organomet. Chem.*, 1982, **240**, C1.

6 L. M. Engelhardt, W-P. Leung, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1983, 386.

7 von K. Andrä and F. Fleischer, *Z. Anorg. Allg. Chem.*, 1982, **485**, 210.

8 *e.g.* A. G. Olivero, B. Weidmann, and D. Seebach, *Helv. Chim. Acta*, 1981, **64**, 2485.

9 B. J. Wakefield, in ' Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 7.

10 M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 14.

11 L. M. Engelhardt, M. F. Lappert, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 1323.

12 J. Klein, A. Medlik, and A. Y. Meyer, *Tetrahedron*, 1976, **32**, 51.

13 E. Dunkelblum and H. Hart, *J. Org. Chem.*, 1979, **44**, 3482.

14 P. C. Jones and R. West, *J. Am. Chem. Soc.*, 1968, **90**, 2656.

15 R. Noyori, N. Sano, S. Murata, Y. Okamoto, H. Yuki, and T. Ito, *Tetrahedron Lett.*, 1982, **23**, 2969.

16 W. Neugebauer, A. J. Kos, and P. von Ragué Schleyer, *J. Organomet. Chem.*, 1982, **228**, 107; U. Schubert, W. Neugebauer, and P. von Ragué Schleyer, *J. Chem. Soc., Chem. Commun.*, 1982, 1184.

17 O. W. Steward and J. S. Johnson, *J. Organomet. Chem.*, 1973, **55**, 209.

18 R. P. Zerger and G. D. Stucky, *J. Chem. Soc., Chem. Commun.*, 1973, 44.

19 J. J. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, 1972, **94**, 7333.

20 M. Daney, R. Lapouyade, B. Labrande, and H. Bouas-Laurent, *Tetrahedron Lett.*, 1980, **21**, 153.

21 E. W. Colvin, ' Silicon in Organic Synthesis,' Butterworths, London, 1981, p. 30.

22 J. J. Eisch and M-R. Tsai, *J. Organomet. Chem.*, 1982, **225**, 5.

23 R. Amstutz, J. D. Dunitz, and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 465.

24 M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, unpublished work.

25 G. E. Hartwell and A. Allerhand, *J. Am. Chem. Soc.*, 1971, **93**, 4415.

26 *Cf.*, G. E. Coates, M. L. H. Green, and K. Wade, ' Organometallic Compounds,' Methuen, London, 1967, vol. 1, p. 78.

27 D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 1950, 711.

28 von G. Wittig, G. Koenig, and K. Clauss, *Anal. Chem.*, 1955, **593**, 127.

29 ' International Tables for *X*-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

30 ' The X-RAY System, Version of March, 1976,' Technical Report TR-446, ed. J. M. Stewart, Computer Science Center, University of Maryland.

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