Synthesis of α-Lithioarylmethanes of *m*-Xylene and its α-Trimethylsilyl Derivatives; Crystal Structure of [{Li($Me_2NCH_2CH_2NMe_2$)}$_2${C_6H_4($CHSiMe_3$)$_2$-*m*}] †

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Crystalline organolithium complexes [{Li(pmdien)}{$C_6H_4(CH_2R)(CHR')$-*m*}] (R = R′ = H, R = R′ = $SiMe_3$, pmdien = *NNN′N″N″*-pentamethyldiethylenetriamine), [{Li(tmen)}{$C_6H_4Me(CHSiMe_3)$-*m*}] (tmen = *NNN′N′*-tetramethylethylenediamine), and [{Li(tmen)}$_2${$C_6H_4(CHSiMe_3)_2$-*m*}] have been prepared by the metallation of *m*-xylene or the appropriate α-silylated *m*-xylene using $LiBu^n$–tertiary amine in hexane at *ca.* 20 °C. Lithiation of $C_6H_4Me[CH(SiMe_3)_2]$-*m* and $C_6H_4(CH_2SiMe_3)[CH(SiMe_3)_2]$-*m* using $LiBu^n$(tmen) yielded respectively –*CH*$(SiMe_3)_2$ and –*CH*$_2SiMe_3$ metallated species (not isolated) whereas $C_6H_4[CH(SiMe_3)_2]_2$-*m* is unaffected under the same conditions. The crystal structure of the compound [{Li(tmen)}$_2${$C_6H_4(CHSiMe_3)_2$}]-*m* has been determined and shows two non-equivalent lithium centres. One lithium is η^2 bonded to the hydrocarbyl moiety, interacting through a carbon bearing a $-SiMe_3$ group [2.14(1) Å] and its nearest carbon [2.30(1) Å], the other Li is η^3 bonded, on the opposite side of the C_8 plane, with Li–C distances of 2.14(1) Å to the other carbon bearing a $SiMe_3$ group, 2.26(1) Å to its adjacent carbon, and 2.44(1) Å to the next.

In a recent paper we reported lithium alkyl complexes derived from α-metallation reactions of α-trimethylsilyl-*p*-xylenes, together with the synthesis and reactions of the di-Grignard reagent of 1,4-bis(chloromethyl)benzene.[1] The metallation reactions differ from analogous reactions of the *o*-xylene compounds[2] only where the close proximity of the benzylic carbon in the *ortho* case favours either a 1,4 intramolecular anionic silyl migration, intermolecular exchange, for the case of [{Li(pmdien)}($CH_2C_6H_4Me$-*o*)] (pmdien = *NNN′N″N″*-pentamethyldiethylenetriamine) yielding the corresponding benzyl complex [{Li(pmdien)}($CH_2C_6H_5$)] with toluene (thought to originate from release of steric strain), or steric control of metallation. In this paper we extend the study to related reactions of the *meta* system which is in principle free of steric constraints but with electronic effects dissimilar to both previously studied systems.

Dilithium complexes containing *o*- or *p*-[$C_6H_4(CHSiMe_3)_2$]$^{2-}$ differ in the nature of the Li–anion interaction but in both there is a substantial contribution from a quinodimethide resonance form.[1,2] For the *meta*-isomeric dianion this is ruled out and in an attempt to define the characteristics of the dianion, the mode of Li–anion interaction, and which of several possible isomers is present in the solid, a structure determination of [{Li(tmen)}$_2${$C_6H_4(CHSiMe_3)_2$-*m*}] (tmen = *NNN′N′*-tetramethylethylenediamine) has been undertaken and the results are reported herein. For the neutral *m*-xylylene species [$C_6H_4(CH_2)_2$-*m*], also void of a quinodimethide contribution, the ground state, based on theoretical studies, is a triplet.[3]

An objective of this study was to develop suitable organolithium compounds as transfer reagents for substituted benzyl anionic species and for *m*-xylenediyl and/or its α-trimethylsilylated analogues. *m*-Xylenediyl-containing reagents are of interest in preparing binuclear metal complexes, of which to our knowledge the only example is $C_6H_4(CH_2SnMe_3)_2$-*m*.[4] This was prepared from a di-Grignard reagent (**1**) (Scheme 1), which was generated using the optimum conditions for that of the *ortho*-isomeric di-Grignard.[5] The corresponding *para* isomer, $C_6H_4(CH_2SnMe_3)_2$-*p*, has been prepared from a Grignard *in situ* trapping reaction.[4,6] Only a few other examples of *p*-xylenediyl metal complexes have been reported. In contrast to the paucity of both *p*- and *m*-xylenediyl metal derivatives there are numerous examples for the *o*-xylenediyl case,[7] and a major portion of these originated from the availability of main group transfer reagents.[5,8]

Results and Discussion

Metallation reactions of *m*-xylene and its α-trimethylsilylated compounds using $LiBu^n$(tmen) or $LiBu^n$(pmdien) are depicted in Schemes 1 and 2. With the exception of reactions yielding (**7**) and (**13**) a highly crystalline and extremely air-sensitive α-lithioarylmethane was obtained. These have been characterized by ^1H and ^{13}C n.m.r. and for one, compound (**3**), a crystal structure determination. In all cases the position of lithiation has been clarified by characterizing air-stable trimethylsilyl derivatives or in one case a methyl derivative.

Metallation of *m*-xylene, using $LiBu^n$ and tmen in varying ratios, has been reported previously. Mixtures of organolithium species were noted in all reactions, clearly demonstrating the inadequacy of $LiBu^n$(tmen) for selective mono- or di-lithiation.[9] We find that one or more equivalents of $LiBu^n$–pmdien in a 1:1 ratio yields almost quantitatively, based on *m*-xylene, the monolithiated species, (**9**). This contrasts with a high-yield dimetallation using the more reactive reagent $Na(CH_2CMe_3)$(tmen).[10] Surprisingly for *p*- and *o*-xylene this reagent afforded a monometallated species, and a mixture of mono- and di-α-metallated species respectively.[10] Other, more recent reagents, potential sources of the *m*-xylenediyl dianion, are a di-Grignard,[4] (**1**), the product of $LiBu^n$–$KOBu^t$ with *m*-xylene (quantitative)[11] and that derived from $LiBu^n$–$KOCHMeCH_2CH_2Me$ and 1-methyl-3-methylenecyclohexane.[12] Of these the di-Grignard should prove more versatile owing to the likelihood of lower relative reducing potential compared with Group 1A arylmethane compounds.

On attempting to recrystallize compound (**9**) from toluene

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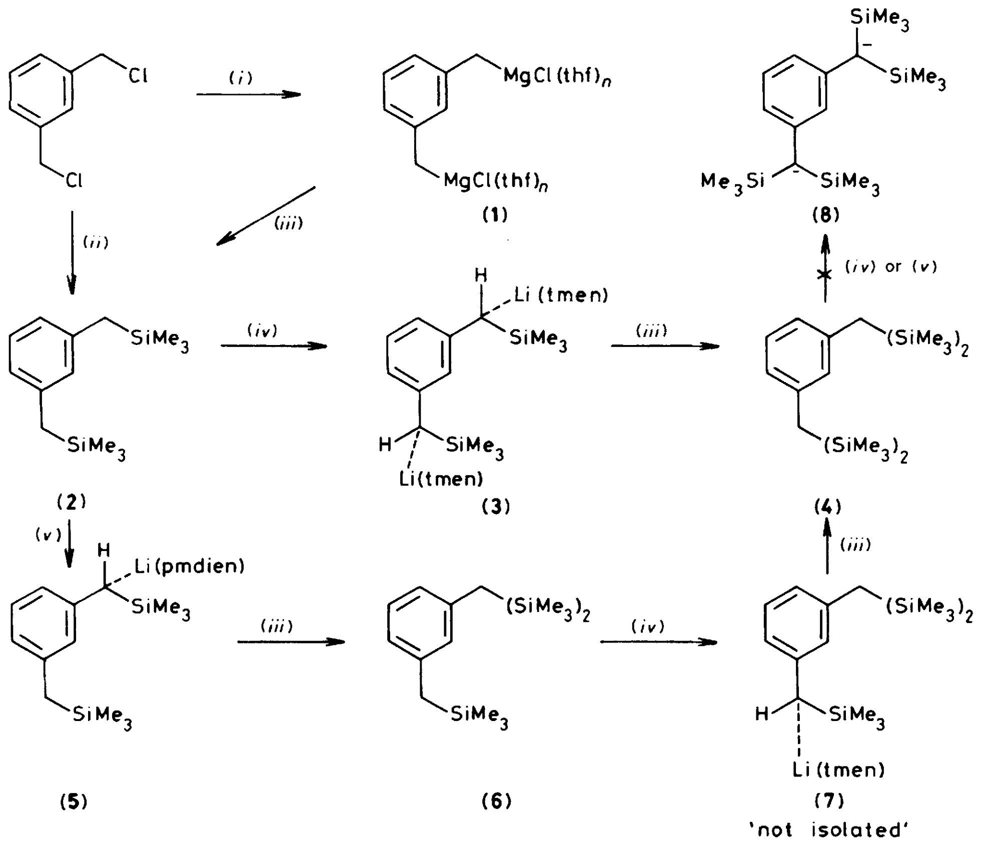
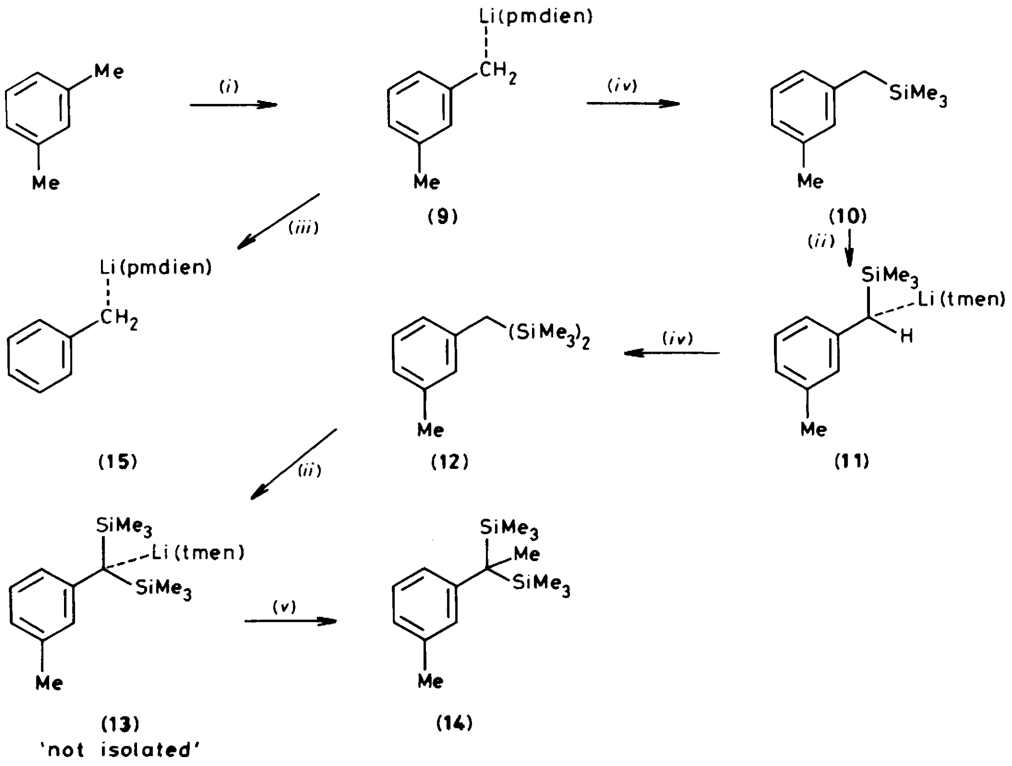
† α,α′-Bis[(*NNN′N′*-tetramethylethylenediamine)lithio]-α,α′-bis-(trimethylsilyl)-*m*-xylene.

Supplementary data available (No. SUP 56088, 5 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: mmHg ≈ 133 pa.



Scheme 1. Reagents and conditions: (*i*) Mg, thf; (*ii*) Mg, thf, $SiMe_3Cl$; (*iii*) $SiMe_3Cl$; (*iv*) $LiBu^n$ (1.6 mol l^{-1} in hexane) + tmen; (*v*) $LiBu^n$ (1.6 mol l^{-1} in hexane) + pmdien



Scheme 2. Reagents and conditions: (*i*) $LiBu^n$ (1.6 mol l^{-1} in hexane) + pmdien *or* tmen for (*ii*); (*iii*) recrystallize from toluene; (*iv*) $SiMe_3Cl$; (*v*) MeI, hexane

an exchange reaction was evident, yielding [{Li(pmdien)}-($CH_2C_6H_5$)] (**15**) (Scheme 2). A similar result was noted for the *ortho* isomeric compound but not for the *para* analogue and because of a similar electronic effect for *ortho*- and *para*-methyl ring substituents the exchange for the former was attributed to relief of steric strain.[2] For the *meta* case steric effects are negligible and the cause of exchange is the electron releasing property of the methyl group in the anion $^{-}CH_2C_6H_4Me$-*m* making that anion more basic than the benzyl anion.

For the trimethylsilylated *m*-xylenes the position of metallation(s) was in accordance with established relative thermodynamic acidities,[3,13] *viz.* R-CH_3 < RCH_2SiMe_3 < R$CH(SiMe_3)_2$ (R = aryl), except for compounds (**4**) and (**6**) (Scheme 1). Metallation of (**2**) was found to be similar to the *ortho* and *para* analogues with the isolation in modest yield of a dilithio-species, (**3**), using two equivalents of LiBu^n(tmen) and with the structure reported herein all three isomeric dilithio-species have now been structurally authenticated. With two equivalents of LiBu^n(pmdien) a mixture of mono- and di-lithio-species was established by quenching reaction mixtures with $SiMe_3Cl$ and identifying products using g.c. mass spectra. This is similar to the behaviour of both the *para*[1] and *ortho*[2] isomers. Steric control of dimetallation as in the *ortho* case, due to the close proximity of $\overline{C}H(SiMe_3)$[Li(pmdien)] to *o*-CH_2SiMe_3, is thus minimal. Using one equivalent of LiBu^n(pmdien), however, there is selective monolithiation of (**2**), and its *ortho*[2] and *para*[1] isomers.

For the conditions studied metallation of compounds (**4**) and (**6**) failed to yield species formed by loss of the most acidic proton, those attached to a carbon atom bearing two bulky trimethylsilyl substituents. Steric factors are possibly controlling the course of the reaction in these compounds. In addition to using LiBu^n(tmen) and LiBu^n(pmdien) to metallate (**4**) with a view of forming the dianion, (**8**), a reasonable goal on electronic grounds since (**3**) is readily formed, we have also investigated its treatment with other recognized metallating reagents, including LiMe–OEt_2–tetrahydrofuran (thf), which is effective for the formation of Li[C$(SiMe_3)_3$] from $CH(SiMe_3)_3$,[14] but to no avail. It is noteworthy that metallation of $CH(SiMe_3)_3$ using a bidentate Lewis base, tmen, with LiBu^t affords a Si–CH_3 metallated species.[14] A compound related to (**4**), $C_6H_5CH(SiMe_3)_2$, is also resistant to metallation at the tertiary carbon centre,[15] whereas its isoelectronic compound $C_5H_4N[CH(SiMe_3)_2]$-2 is readily deprotonated at that centre.[15] However, the nitrogen may facilitate metallation by complexation to lithium and/or impose less hindrance than a C(aromatic)–H group.

The difference in the site of metallation of (**6**) and (**12**) is unusual but is consistent with that of the related *para* compounds.[1] In the light of the inability to generate (**8**) we propose that the first step on metallation of (**12**) is R–CH_3 metallation followed by a migration to yield (**13**), the formation of which was established by the isolation of the methylated compound, (**14**) (Scheme 2). Metallation of the *ortho* isomeric compound of (**12**) yields a proposed R–CH_3 metallated intermediate but this rearranges *via* a 1,4-anionic silyl migration to give [{Li(pmdien)}{$C_6H_4(CH_2SiMe_3)(CHSiMe_3)$-*o*}].[2] This and other migrations are thought to be intramolecular involving a five-co-ordinate silicon intermediate.[16] If R–CH_3 metallation is the initial metallated species of (**12**), there is little prospect for silyl migration because of the inability to achieve such an intermediate. None of compound (**2**), the product of migration, was evident on treating the organolithium solution with aqueous HCl.

The presence of a trimethylsilyl group on the carbon *meta* to $CH(SiMe_3)_2$ may stabilize the generated anion, (**7**), with respect to formation of the tertiary carbon metallated species, possibly because of the π-acidity of the α-silyl group and some steric restrictions on the alternative –$CH(SiMe_3)_2$ lithiated species.

The α-silylated *m*-xylene compounds (**4**) and (**6**) are new. Compound (**2**) has been prepared in high yield by four routes, two involving quenching of *o*-xylenediyl reagents mentioned above,[11,12] another by quenching the di-Grignard, (**1**), with $SiMe_3Cl$ (Scheme 1),[4] and finally by an *in situ* Grignard trapping reaction (Scheme 1) for which the yield and full details were not reported.[17] In our hands the condition of refluxing the resulting mixture for 3—5 h was found to be unnecessary.

Structural Commentary.—The structure determination establishes the solid to comprise discrete aggregates of (**3**). Results

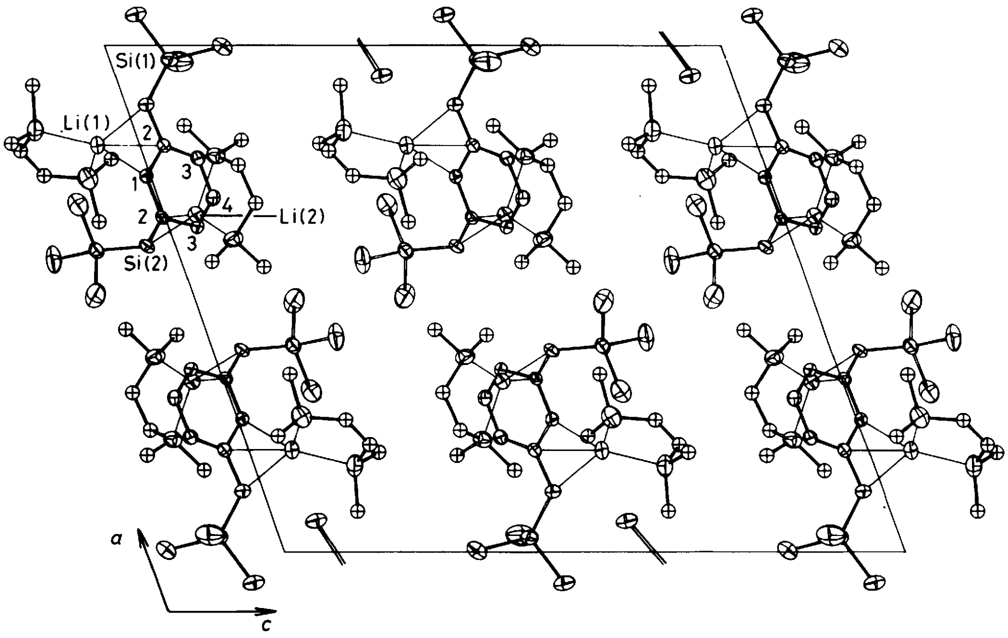


Figure 1. Non-hydrogen atom unit-cell contents of (**3**) projected down *b*

Table 1. Non-hydrogen atomic co-ordinates

	Ligand (section 1)			Ligand (section 2)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Li	0.800 7(6)	0.219 4(11)	−0.069 2(5)	0.664 8(6)	−0.136 7(11)	0.050 9(5)
Aromatic ligand						
C(1)	0.739 8(4)	0.071 2(5)	−0.007 3(3)			
C(2)	0.800 4(4)	0.151 2(5)	0.038 7(3)	0.658 8(3)	0.056 3(5)	−0.005 4(3)
C(3)	0.775 1(4)	0.228 1(6)	0.086 3(3)	0.640 7(3)	0.132 3(6)	0.046 2(3)
C(4)	0.697 5(4)	0.216 2(6)	0.088 7(3)			
C(5)	0.881 5(3)	0.160 6(5)	0.033 4(3)	0.602 8(3)	−0.038 3(5)	−0.046 5(3)
Si	0.971 1(1)	0.230 5(2)	0.097 6(1)	0.594 0(1)	−0.105 6(2)	−0.131 50(8)
C(6)	0.997 3(4)	0.162 1(9)	0.190 5(3)	0.684 1(5)	−0.196 8(7)	−0.134 6(4)
C(7)	1.060 9(4)	0.201 2(9)	0.068 3(4)	0.576 1(5)	0.011 8(8)	−0.206 6(3)
C(8)	0.967 2(5)	0.405 6(8)	0.110 6(5)	0.504 9(5)	−0.215 0(10)	−0.159 2(4)
tmen ligand						
C(12)	0.804 6(5)	0.112 3(9)	−0.208 5(4)	0.810 8(5)	−0.096 3(9)	0.167 0(4)
C(13)	0.920 0(8)	0.226 7(14)	−0.141 1(5)	0.840 1(5)	−0.221 4(9)	0.083 0(4)
N(1)	0.830 8(4)	0.219 6(7)	−0.162 2(3)	0.779 6(3)	−0.196 4(6)	0.116 5(3)
C(11)	0.789 5(13)	0.330 7(11)	−0.198 1(6)	0.761 3(6)	−0.309 6(9)	0.147 6(6)
C(21)	0.741 1(7)	0.402 4(13)	−0.173 4(7)	0.687 1(6)	−0.328 4(9)	0.154 1(5)
N(2)	0.735 1(4)	0.378 3(6)	−0.103 6(3)	0.616 4(4)	−0.276 5(7)	0.097 3(3)
C(22)	0.773 2(7)	0.478 3(9)	−0.054 8(6)	0.572 6(7)	−0.370 9(11)	0.049 7(6)
C(23)	0.650 4(6)	0.365 1(9)	−0.110 1(4)	0.562 0(6)	−0.218 4(11)	0.130 2(5)

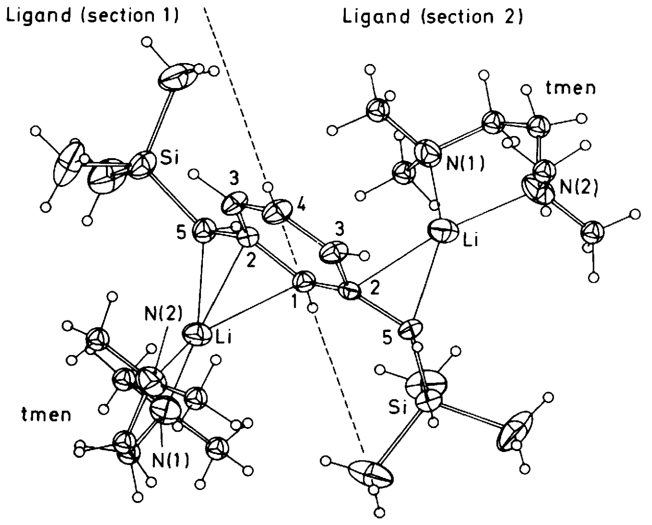
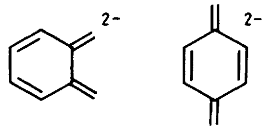


Figure 2. A single molecule of (3) showing 20% ellipsoids, as in Figure 1, and hydrogen atoms at an arbitrary radius of 0.1 Å. Arbitrary radii are also employed for the tmen carbon atoms, whose thermal motion is abnormally high

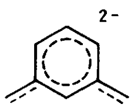
Table 2. Non-hydrogen distances (Å)

	Ligand (section 1)	Ligand (section 2)
Aromatic ligand		
C(1)–C(2)	1.416(7)	1.430(9)
C(2)–C(3)	1.423(9)	1.416(9)
C(2)–C(5)	1.452(9)	1.438(7)
C(3)–C(4)	1.371(11)	1.379(8)
C(5)–Si	1.803(5)	1.790(6)
C(6)–Si	1.886(8)	1.854(8)
C(7)–Si	1.866(8)	1.880(8)
C(8)–Si	1.865(9)	1.858(10)
tmen ligands		
C(11)–N(1)	1.43(1)	1.43(1)
C(12)–N(1)	1.43(1)	1.43(1)
C(13)–N(1)	1.46(2)	1.45(1)
C(11)–C(21)	1.34(2)	1.35(2)
C(21)–N(2)	1.45(2)	1.46(1)
C(22)–N(2)	1.43(1)	1.41(1)
C(23)–N(2)	1.44(1)	1.45(1)
Lithium environment		
Li–C(5)	2.14(1)	2.14(1)
Li–C(2)	2.26(1)	2.30(1)
Li–C(1)	2.44(1)	2.97(1)
Li–C(3)	—	2.86(1)
Li–N(1)	2.08(1)	2.08(1)
Li–N(2)	2.01(1)	2.06(1)

are shown in Tables 1—3, and Figures 1 and 2. The asymmetric unit is one complete molecule and, unlike the *ortho*[2] and *para*[1] isomeric species, it is devoid of symmetry. Both the *ortho* and *para* molecules show a contribution from a quinodimethide resonance form (**I**). This is symmetry forbidden in the *meta* case, although bond distances within the aromatic plane and for the adjacent benzylic carbons show evidence of extensive delocalization, (**II**), conforming to the potential *mm* symmetry on which the numbering scheme (see below) is based.



(I)



(II)

The bond distances C(1)–C(2) [1.416(7), 1.430(9) Å (sections 1 and 2, defined in the Experimental section)] and C(2)–C(3) [1.423(9), 1.416(9) Å (sections 1 and 2)] are above the usual C(aromatic)–C(aromatic) distance of 1.40 Å, whereas C(3)–C(4) [1.371(11), 1.379(8) Å (sections 1 and 2)] are significantly less; C(2)–C(5) [1.452(9), 1.438(7) Å] compare with 1.49 Å for a normal C(aromatic)–C(sp^3) distance. The geometry about C(5) is closer to that of C(sp^2) requirements than C(sp^3) and the C(5)–Si distances [1.803(5) and 1.790(6) Å] are shorter

Table 3. Non-hydrogen angles (°)

	Ligand (section 1)	Ligand (section 2)
Aromatic ligand		
C(2)–C(1)–C(2)	124.9(5)	
C(1)–C(2)–C(3)	116.0(6)	114.7(5)
C(1)–C(2)–C(5)	121.4(5)	123.0(5)
C(3)–C(2)–C(5)	122.4(5)	121.9(6)
C(2)–C(3)–C(4)	119.9(5)	121.1(6)
C(3)–C(4)–C(3)	123.1(6)	
C(2)–C(5)–Li	75.4(4)	77.6(4)
Si–C(5)–Li	133.5(4)	121.2(4)
C(2)–C(5)–Si	127.1(4)	129.4(5)
C(5)–Si–C(6)	113.7(3)	115.6(3)
C(5)–Si–C(7)	108.9(3)	115.3(3)
C(5)–Si–C(8)	116.0(3)	108.7(4)
C(6)–Si–C(7)	106.9(3)	103.2(4)
C(6)–Si–C(8)	104.5(4)	107.3(4)
C(7)–Si–C(8)	106.2(4)	105.9(4)
tmen ligands		
C(11)–N(1)–C(12)	109.2(7)	113.6(7)
C(11)–N(1)–C(13)	113.9(11)	110.5(7)
C(11)–N(1)–Li	102.0(9)	102.5(6)
C(12)–N(1)–Li	116.7(7)	105.9(6)
C(13)–N(1)–Li	107.8(6)	117.3(5)
C(12)–N(1)–C(13)	107.5(8)	107.2(6)
C(21)–N(2)–C(22)	110.7(9)	112.1(7)
C(21)–N(2)–C(23)	109.5(7)	108.3(7)
C(22)–N(2)–C(23)	110.9(8)	108.3(8)
C(21)–N(2)–Li	104.8(7)	104.4(6)
C(22)–N(2)–Li	107.6(6)	114.5(7)
C(23)–N(2)–Li	113.3(6)	109.1(7)
N(1)–C(11)–C(21)	123.3(13)	121.5(8)
N(2)–C(21)–C(11)	120.6(11)	116.8(9)
Lithium environment		
N(1)–Li–N(2)	89.0(5)	87.4(5)
N(1)–Li–C(5)	124.3(6)	143.0(7)
N(2)–Li–C(5)	132.8(6)	126.4(5)
C(2)–Li–C(5)	38.4(3)	37.5(3)
C(2)–Li–N(1)	157.2(6)	116.6(5)
C(2)–Li–N(2)	113.8(6)	152.6(6)

than the mean Si–CH_3 (1.868 Å), suggestive of a contribution from Si(*d*π)–C(*p*π) bonding. (The Si–C distances are similar to those of the *ortho*- and *para*- isomeric compounds,[1,2] and $[\{Li(tmen)\}_2\{[CH(SiMe_3)C_6H_4\text{-}o]_2\}]$.[18]) Even so, the angles of the exocyclic carbon atoms are enlarged well above the trigonal value, 127.1, 129.4° *cf.* 130.0[2] and 127.2°[1] for the *ortho* and *para* analogues respectively, possibly a consequence of relief of steric strain between –$SiMe_3$ and the nearest ring proton. This large angle may explain the lack of dilithiation of (**4**). In $[\{Li(pmdien)\}\{CH(SiMe_3)_2\}]$ the Si–C–Si angle is 124(2)°[13] and if this is considered in conjunction with the large Si–C–C (aromatic) angle in (**3**), unfavourable non-bonding interactions for a trigonal benzylic carbon bearing two trimethylsilyl substituents are likely. However a torsion of the trigonal plane relative to the aromatic plane or the benzylic carbon becoming pyramidal would accommodate these large angles. Either effect may be in operation in compound (**13**).

The aromatic ring carbon atoms in (**3**) are almost planar (σ 0.02 Å, χ^2 43.6); silicon atoms deviate 0.41 and −0.42 Å from the plane and the associated lithium atoms −1.81 and 2.16 Å. The benzylic carbon deviations are 0.01 and 0.13 Å.

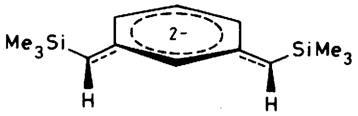
The Li(tmen) portions of the molecule are unexceptional when compared to those of the *ortho*[2] and *para*[1] compounds. Lithium–hydrocarbyl ligand interactions are not new, but it is the first example in which η^3- and η^2-bonding configurations occur within the same molecule.

Li(1) is in close contact with three carbon atoms; C(5,2,1) (section 1) = 2.14(1), 2.26(1) and 2.44(1) Å respectively, all shorter than the values in $[\{Li(tmen)\}_2\{[CH(SiMe_3)C_6H_4\text{-}o]_2\}]$ (2.21, 2.38, and 2.55 Å)[18] and $\{Li[N(CH_2CH_2)_3N](CH_2C_6H_5)\}_n$[19] (2.21, 2.39, and 2.59 Å). Li(2) interacts through two carbon centres, C(5) and C(2) at 2.14(1) and 2.30(1) Å, respectively; the adjacent aromatic carbon atoms C(1) and C(3) lie at distances of 2.97(1) and 2.86(1) Å, respectively, from the lithium. The only other example of an η^2-bonding configuration is for both lithium atoms in the *para* isomer of the present compound,[1] the analogous Li–C distances being 2.38(1) and 2.10(1) Å for Li-C(aromatic) and Li-C_α respectively.[1] Describing η^3 and η^2 bonding as the usual 'contact-ion-pair' type may be incorrect since the Li-C distances are shorter than Li–C in 2-lithio-2-methyl-1,4-dithiane, 2.186 Å, for which electron density maps support a covalent structure.[20] Furthermore, in $[\{Li(pmdien)\}\{CH(SiMe_3)_2\}]$[13] Li–C is short at 2.13 Å and like the previous example is devoid of carbon delocalization effects. The same can be said for $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$[21] and $[Li(thf)\{C(SiMe_2Ph)_3\}]$[22] for which Li–C distances are respectively 2.18(1) and 2.12(2) Å. At the σ(Li–C) interaction limit for benzyl-lithium complexes there are three different types: electron precise compounds, *viz.* $[\{Li(pmdien)\}\{C_6H_4Me(CHSiMe_3)\text{-}o\}]$, Li–$C_\alpha$ 2.26(1) Å ,[2] and 2-lithio-2-phenyl-1,4-dithiane, Li–C_α 2.28 Å;[20] those with multi-centre bonding, found in $\{Li(tmen)\}_2\{(CH_2C_6H_4\text{-}o)_2\}$, Li–$C_\alpha$ 2.30 Å;[18] and an electron deficient compound devoid of electron deficient bonding, $[\{Li[NC_5H_4C(SiMe_3)_2\text{-}2]\}_2]$, Li–$C_\alpha$ 2.213(7) Å.[15] Compounds (**5**) and (**9**) possibly have structures in the σ electron precise category.

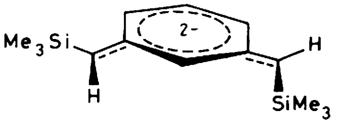
The *ortho*-isomeric compound of (**3**) is a 'contact-ion-pair' structure possessing two η^4-Li centres above and below the *o*-xylenediyl plane at 2.37 Å to the C_α atoms and 2.36 Å to the C(aromatic) atoms. The mode of lithium–anion interaction in complexes (**7**) and (**11**) is possibly of the η^3 'contact-ion-pair' type as is found in the related species $[\{Li(tmen)\}_2\{[CH(SiMe_3)C_6H_4\text{-}o]_2\}]$.[18]

The position of the lithium atoms in the *ortho* and *para*[1] analogues is consistent with them lying above nodes in the highest occupied molecular orbital,[23] in accordance with maximum overlap of the empty lithium orbital. For the *meta* configuration two occupied orbitals of similar energy lack a node between C(5) and C(2).[24] However, the energy and nature of the levels will be perturbed by the trimethylsilyl groups.

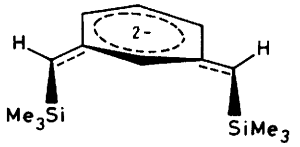
Only one of three theoretically possible isomers, (**III**)—(**V**), for the disposition of trimethylsilyl groups is found in the *solid, i.e.* (**IV**). The nature of the species present in solution has also



(III)



(IV)



(V)

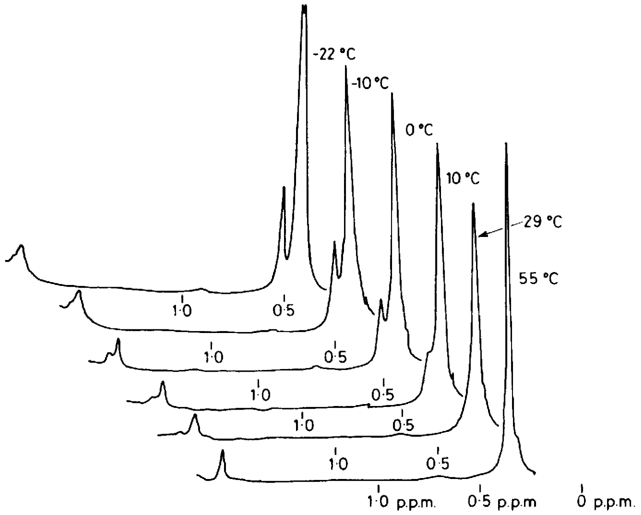


Figure 3. Variable-temperature ^{1}H n.m.r. spectra of the $-SiMe_3$ and $C\mathit{H}SiMe_3$ regions of compound (**3**), recorded in [$^2H_8$]toluene at 90 MHz

been investigated, using variable-temperature ^{1}H n.m.r. spectroscopy. On cooling a toluene solution of (**3**) below ambient temperature two changes were evident. Low-field $-C\mathit{H}SiMe_3$ and $-SiMe_3$ resonances developed followed by a splitting of the major $-SiMe_3$ peak (Figure 3). (Unfortunately the $-C\mathit{H}SiMe_3$ resonance region was obscured by those of tmen at low temperature.) The small low-field peaks correspond to either of the symmetrical isomers, (**III**) and (**V**), and the others to isomer (**IV**) for which the $-SiMe_3$ groups are expected to be non-equivalent. At high temperature rapid interconversion between the various isomers on the n.m.r. time-scale is proposed. The low-temperature ^{6}Li n.m.r. spectrum[25] has two resonances in accordance with the presence of two isomers in solution, (**III**) or (**V**), and (**IV**), but with the Li(tmen) moieties fluxional on the hydrocarbyl group within each isomer. Of the two symmetrical isomers (**V**) may be unfavourable due to steric crowding in the vicinity of the approach of the *cis*-$SiMe_3$ groups, which is suggested by molecular models. The mode of interaction of the hydrocarbyl group with the metal centres and/or repulsion between methyl groups of the tmen ligands and $-SiMe_3$ groups, however, are likely to be important factors in determining the orientation of the methylene substituents, both in solution and in the solid.

Experimental

General Procedures.—Owing to the air-sensitivity of all the lithium complexes, $SiMe_3Cl$, and the Grignard reagent, (**1**), 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 tetrahydrofuran (thf)], CaH_2 (hexane), and sodium metal (diethyl ether).

Materials.—Compound (**2**) was prepared according to the literature procedures.[4,16] 1,3-Bis(chloromethyl)benzene was recrystallized from hexane. The ligands tmen and pmdien were purified by distillation over KOH. Methyl iodide was dried over $CaCl_2$ and distilled under a dinitrogen atmosphere.

Physical and Analytical Measurements.—Elemental (C and H) analyses of the lithium alkyl derivatives were performed by the Australian Mineral Development Laboratories, Melbourne. Hydrogen-1 n.m.r., carbon-13 n.m.r., and mass spectra were recorded on Hitachi–Perkin-Elmer R-24B (60 MHz) or Brüker HX90 (90 MHz), Brüker WP-80 (20.1 MHz), and HP-5986 spectrometers respectively.

Preparation of $[\{Li(tmen)\}_2\{C_6H_4(CHSiMe_3)_2\text{-}m\}]$, (**3**).—To a solution of (**2**) (0.88 g, 3.5 mmol) and $LiBu^n$ in hexane (4.8 cm^3, 1.6 mol l^{-1}, 7.7 mmol) at 0 °C was added tmen (1.2 cm^3, 7.7 mmol). The resulting yellow solution was kept at room temperature overnight yielding yellow crystals of the *title compound*. They were filtered off, washed with cold (*ca.* −20 °C) pentane (2×5 cm^3), and dried *in vacuo*. Yield 1.23 g (71%), m.p. 117 °C; ^{1}H n.m.r. (90 MHz, C_7D_8), δ 0.36 (18 H, s), 1.67 (2 H, s), 1.90 (8 H, s), 2.05 (24 H, s), 6.7 (4 H, m); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), δ 3.37 (Me_3Si), 43.85 (CHSi), 45.04 (Me_2–N), 56.26 (CH_2–N), 101.98, 103.63, 131.59, 156.70 (C_6H_4).

Preparation of $C_6H_4[CH(SiMe_3)_2]_2\text{-}m$, (**4**).—To an ice-cooled solution of (**3**) in hexane (2.40 g, 4.85 mmol in 100 cm^3) was added $SiMe_3Cl$ (1.30 g, 12 mmol). The mixture was stirred for 2 h at room temperature, whereupon 2 mol l^{-1} HCl was added (20 cm^3) and the hexane solution separated, washed with water (50 cm^3), and dried over $MgSO_4$ overnight. Removal of solvent *in vacuo* afforded white crystals of the *title compound*. Yield 1.35 g (70%), m.p. 61 °C (Found: C, 59.85; H, 10.90. $C_{20}H_{42}Si_4$ requires C, 60.80; H, 10.70%); ^{1}H n.m.r. (60 MHz, $CDCl_3$), δ −0.1 (36 H, s), 1.28 (2 H, s), 6.39, 6.60 (4 H, m); ^{13}C n.m.r. (^{1}H decoupled, $CDCl_3$), δ 0.66 (Me_3Si), 30.16 (CH), 124.27, 128.26, 129.74, 143.34 (C_6H_4). Mass spectrum (*m*/*e*): 394 $[P]^+$, 379 $[P-Me]^+$, 321 $[P - SiMe_3]^+$, and 248 $[P - 2\ SiMe_3]^+$.

Preparation of $[\{Li(pmdien)\}\{C_6H_4(CH_2SiMe_3)(CHSiMe_3)\text{-}m\}]$, (**5**).—To an ice-cooled solution of (**2**) (1.0 g, 4 mmol) and pmdien (0.75 g, 4.3 mmol) was added $LiBu^n$ in hexane (2.8 cm^3, 1.6 mol l^{-1}, 4.5 mmol). The yellow solution was stored at room temperature for 18 h. Yellow crystals of the *title compound* were isolated by a similar method to that for (**3**). Yield 1.56 g (91%), m.p. 81 °C; ^{1}H n.m.r. (60 MHz, C_6D_6), δ 0.26 (9 H, s), 0.49 (9 H, s), 1.68 (1 H, s), 1.82 (2 H, s), 1.98 (8 H, s), 2.03 (12 H, s), 2.1 (3 H, s), 6.06, 6.51, 6.9 (4 H, m); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), δ −1.13 (Me_3Si), 3.25 (Me_3Si), 27.51 (CH_2), 39.92 (CH), 44.23 (Me–N), 45.73 (Me_2N), 53.81 (CH_2–N), 57.46 (CH_2–N), 109.72, 116.90, 120.14, 138.76, 159.03 (C_6H_4).

Preparation of $C_6H_4(CH_2SiMe_3)[CH(SiMe_3)_2]\text{-}m$, (**6**).—The procedure was the same as for preparation of (**4**), the product being purified by distillation (b.p. 90—92 °C, 0.2 mmHg). Yield of the *title compound* (**6**) from (**5**) (1.62 g) was 0.8 g (66%) (Found: C, 63.25; H, 10.70. $C_{17}H_{34}Si_3$ requires C, 63.25; H, 10.65%); ^{1}H n.m.r. (80 MHz, $CDCl_3$), δ 0.06 (9 H, s), 0.11 (18 H, s), 1.49 (1 H, s), 2.09 (2 H, s), 6.67, 6.78, 7.01, 7.10 (4 H, m); ^{13}C n.m.r. (^{1}H decoupled, $CDCl_3$), δ −1.39 (Me_3Si), 0.55 [$(Me_3Si)_2$], 27.37 (CH_2), 29.87 (CH), 123.64, 124.78, 128.20, 128.88, 140.38, 143.17 (C_6H_4).

Preparation of (**4**) *from* (**6**).—To a solution of (**6**) (0.5 g, 1.55 mmol) and $LiBu^n$ in hexane (1.0 cm^3, 1.6 mol l^{-1}, 1.6 mmol) at 0 °C was added tmen (0.24 cm^3, 1.6 mmol). After 3 h at room temperature, to the resulting yellow solution was added a hexane solution of $SiMe_3Cl$ (0.20 g in 30 cm^3). The mixture was then stirred at room temperature for 1 h, after which the product was isolated by the method described above. Yield 0.35 g (57%).

Preparation of $[\{Li(pmdien)\}(CH_2C_6H_4Me\text{-}m)]$, (**9**).—To an ice-cooled solution of pmdien (9.0 g, 52 mmol) and $LiBu^n$ in hexane (32 cm^3, 1.6 mol l^{-1}, 52 mmol) was added *m*-xylene (5.0 g, 47 mmol). The yellow solution was stored at room temperature for 1 h during which yellow crystals of the *title compound* precipitated. These were filtered off, washed with cold (*ca.* −20 °C) pentane (2 × 5 cm^3) and dried *in vacuo* (yield 11.8 g, 88%), m.p. 114—116 °C; ^{1}H n.m.r. (60 MHz, C_6D_6), δ 1.96 (23 H, s), 2.14 (2 H, s), 2.18 (3 H, s), 5.84, 6.32, 6.77 (4 H, m); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), δ 21.11 (Me), 36.68 (CH_2), 44.08 (Me_2N), 45.56 (Me–N), 54.15 (CH_2–N), 57.46 (CH_2–N), 106.31, 114.39, 117.30, 129.14, 136.16, 159.79 (C_6H_4).

Preparation of $C_6H_4Me(CH_2SiMe_3)$-*m*, **(10)**.—The procedure was as for the preparation of **(6)** from **(5)**. Yield of the *title compound* 68%, b.p. 178 °C (Found: C, 73.70; H, 9.80. $C_{11}H_{18}Si$ requires C, 74.10; H, 10.15%); ^{1}H n.m.r. (60 MHz, $CDCl_3$), δ −0.02 (9 H, s), 2.00 (2 H, s), 2.25 (3 H, s), 6.75 (4 H, m); ^{13}C n.m.r. (^{1}H decoupled, $CDCl_3$), δ −1.61 (Me_3Si), 21.67 (Me), 27.20 (CH_2), 125.07, 125.52, 128.37, 129.22, 137.76, 140.61 (C_6H_4). Mass spectrum (*m*/*e*): 178 $[P]^+$, 163 $[P - CH_3]^+$, 105 $[P - SiMe_3]^+$.

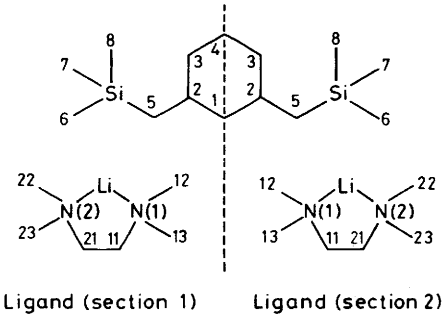
Preparation of $[\{Li(tmen)\}\{C_6H_4Me(CHSiMe_3)$-*m*$\}]$, **(11)**.—To an ice-cooled solution of **(10)** (1.40 g, 7.85 mmol) and $LiBu^n$ in hexane (5.4 cm^3, 1.6 mol l^{-1}, 8.6 mmol) was added tmen (1.3 cm^3, 8.6 mmol). The yellow solution was kept at room temperature for 18 h during which yellow-orange crystals of the *title compound* precipitated. These were isolated by a similar method to that for **(3)**. Yield 2.05 g (87%), m.p. 59—61 °C; ^{1}H n.m.r. (60 MHz, C_6D_6), δ 0.40 (9 H, s), 1.68 (4 H, s), 1.77 (12 H, s), 1.86 (1 H, s), 2.15 (3 H, s), 5.98, 6.45, 6.75 (4 H, m); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), δ 2.68 (Me_3Si), 22.10 (Me), 41.74 (CH), 44.70 (Me_2–N), 56.09 (CH_2–N), 110.24, 116.10, 118.95, 130.05, 138.31, 156.41 (C_6H_4).

Preparation of $C_6H_4Me[CH(SiMe_3)_2]$-*m*, **(12)**.—The procedure was as for the preparation of **(6)** from **(5)**. The *title compound* was distilled (b.p. 44 °C, 0.2 mmHg). Yield 73% (Found: C, 67.30; H, 10.65. $C_{14}H_{26}Si_2$ requires C, 67.10; H, 10.75%); ^{1}H n.m.r. (60 MHz, $CDCl_3$), δ −0.01 (18 H, s), 1.40 (1 H, s), 2.24 (3 H, s), 6.69 (4 H, m); ^{13}C n.m.r. (^{1}H decoupled, $CDCl_3$), δ 0.49 (Me_3Si), 21.79 (Me), 29.76 (CH), 124.56, 126.15, 128.26, 130.02, 137.65, 143.23 (C_6H_4). Mass spectrum (*m*/*e*): 250 $[P]^+$, 235 $[P-CH_3]^+$, 162 $[C_6H_4CH(SiMe_3)]^+$.

Preparation of $C_6H_4Me[CMe(SiMe_3)_2]$-*m*, **(14)**.—The procedure was as for the preparation of **(4)** from **(3)**, except that the resulting yellow solution did not yield a crystalline organolithium compound, and it was quenched with MeI. Yield of the *title compound* 66%, b.p. 75 °C (0.2 mmHg) (Found: C, 68.60; H, 10.55. $C_{15}H_{28}Si_2$ requires C, 68.05; H, 10.65%); ^{1}H n.m.r. (60 MHz, $CDCl_3$), δ −0.04 (18 H, s), 1.34 (3 H, s), 2.27 (3 H, s), 6.9 (4, H, m); ^{13}C n.m.r. (^{1}H decoupled, $CDCl_3$), δ −0.59 (Me_3Si), 16.60 (Me), 22.01 (Me), 22.18 ($-\overset{|}{\underset{|}{C}}-$), 124.44, 127.86, 128.20, 137.19, 146.48 (C_6H_4). Mass spectrum (*m*/*e*): 264 $[P]^+$, 249 $[P-Me]^+$, 91 $[P-SiMe_3]^+$, 176 $[MeC_6H_4CSiMe_3]^+$, 161 $[C_6H_4CSiMe_3]^+$.

Crystallography.—Crystal data. $C_{26}H_{56}Li_2N_4Si_2$, M = 494.7, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 17.377(6), b = 10.526(4), c = 19.865(9) Å, β = 109.76(3)°, U = 3 420 Å^3, D_c (Z = 4) = 0.96 g cm^{-3}, F(000) = 1 096, monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ_{Mo} = 1.2 cm^{-1}. Specimen: pseudo-spherical fragment ~0.3 mm diameter in capillary. T = 295 K.

Structure determination. A unique data set was measured within the limit $2\theta_{max.}$ = 45° using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ/θ scan mode. 3 660 Independent reflections were obtained; 1 939 with $I > 3\sigma(I)$ were considered 'observed' and used in the basically 9 × 9 block-diagonal least-squares refinement without absorption correction after solution by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z,U)_H$ were included as constrained estimates. At convergence R, R' were 0.060, 0.071, reflection weights being $[\sigma^2(F_o) + 0.0005 F_o^2]^{-1}$: no abnormal features were observed in a final difference map. Neutral-atom complex scattering factors[26] were used. Computation used the X-RAY system[27] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Atom labelling is as shown below.



Acknowledgements

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