Axially Asymmetric Metal Alkyls. Part 6.[1] Lithiation of 2,2′-Dimethyl-1,1′-binaphthyl and its Trimethylsilylated Compounds, and of 2,2′,6,6′-Tetramethyl-1,1′-biphenyl (Asymmetric Induction): *X*-Ray Crystal Structures of Monomeric [{Li($Me_2NCH_2CH_2NMe_2$)}$_2${(2-$CH_2C_{10}H_6$)$_2$}] and [Li{($Me_2NCH_2CH_2$)$_2$NMe}-{2-CH_2-6-Me(C_6H_3)$_2$-2′,6′-Me_2}]†

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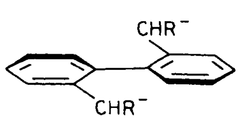
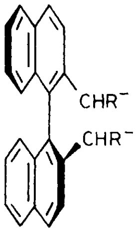
The compound [{Li(tmen)}$_2${(2-$CH_2C_{10}H_6$)$_2$}], (**6**) (tmen = *N,N,N′,N′*-tetramethylethylenediamine), has been prepared *via* metallation, and structurally characterized using *X*-ray diffraction data. It is monomeric with two different lithium centres, one bridging the *ipso*-carbon atoms at 2.13(5) and 2.23(5) Å, the other interacting with one *ipso*-carbon at 2.36(5) Å and its adjacent ring carbon at 2.51 (5) Å, such that one *ipso* carbon is bridging the lithium centres. ^{7}Li N.m.r. data are consistent with this structure in toluene, below *ca.* −28 °C. Treatment of (**6**) with $AsMe_2I$ then MeI yielded the arsonium salt [(2-$Me_3AsCH_2C_{10}H_6$)$_2$]I_2, and with $SiMe_3Cl$ it gave (2-$Me_3SiCH_2C_{10}H_6$)$_2$. This afforded [2-(Me_3Si)$_2CHC_{10}H_6$]$_2$ on treatment with LiBu^n(tmen) then $SiMe_3Cl$. Metallation of 2,2′,6,6′-Tetramethyl-1,1′-biphenyl using LiBu^n(pmdien) (pmdien = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine) in diethyl ether yielded a monolithiated species [{Li(pmdien)}{2-CH_2-6-Me(C_6H_3)$_2$-2′,6′-Me_2}] (**13**), also structurally characterized; the lithium centre is attached to only the *ipso*-carbon of the hydrocarbyl group at 2.14(2) Å. Treatment of the same biphenyl with LiBu^n(sp) [sp = (−)sparteine] in Et_2O yielded a dilithiated species based on the asymmetrical chiral dianion, (2-CH_2-6-MeC_6H_3)$_2^{2-}$. The degree of asymmetric induction in the metallation step was estimated to be *ca.* 40% using a ^{1}H n.m.r.–chiral lanthanide shift reagent technique on the diol (2-$HOCH_2CH_2$-6-MeC_6H_3)$_2$, formed by carboxylation then esterification and reduction of the dilithiated species.

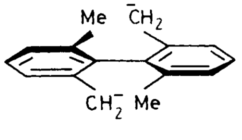
In earlier papers of the current series we concentrated on the development of transfer agents of (2-$CHRC_6H_4$)$_2^{2-}$, (**1**), namely organomagnesium (R = H)[2] and organodilithium (R = H or $SiMe_3$)[3] complexes, and on the chemistry of metallacycles (or heterocycles) derived from these agents, [M{(2-$CHRC_6H_4$)$_2$}], for Main Group 4[3] and transition-metal Group 4,[1,4] 5,[5] and 6[6] elements. Reported herein are the syntheses of organodilithium complexes based on (**2**) (R = H or $SiMe_3$) and (**3**), and selected trimethylsilyl, carboxylic acid, and arsonium salt derivatives. A salient feature of (**2**) and (**3**) is that inversion *via* torsion along the biaryl axis is more energetically unfavourable than for (**1**), and that generating (**3**) *via* dimetallation of 2,2′,6,6′-tetramethyl-1,1′-biphenyl using a chiral metallating reagent can lead to asymmetric induction. This is explored using LiBu^n(sp) [sp = (−)sparteine]. *X*-Ray structure determinations of two of the derived organolithium complexes are also reported as part of an on-going investigation into the nature of lithium–hydrocarbyl interactions. These are difficult to predict and too often the structures of organolithium complexes are over simplified.



(**1**)



(**2**)



(**3**)

We note that reagents based on (**2**) (R = H) have previously been prepared by, (*i*) the metallation of 2,2′-dimethyl-1,1′-binaphthyl using LiBu^n(tmen) (tmen = *N,N,N′,N′*-tetramethylethylenediamine), although the organodilithium complex was not isolated, being treated *in situ* with $SiMe_2Cl_2$, yielding a dimethylsilepine,[7] and (*ii*) the reaction of 2,2′-bis(halogenomethyl)-1,1′-binaphthyls with Mg(ant)(thf)$_3$ in thf (thf = tetrahydrofuran, ant = anthracene), affording di-Grignard reagents.[8] Metallation of optically pure (*R*)- or (*S*)-2,2′-dimethyl-1,1′-binaphthyl[9] is a likely route to optically pure (*R*)- or (*S*)-(**2**). Interestingly, optically pure (*R*)- and (*S*)-2,2′-dilithio-1,1′-binaphthyl[10] and 2,2′-dilithio-6,6′-dimethyl-1,1′-biphenyl[11] have been prepared but they are unstable with respect to racemization at temperatures greater than −44 and −10 °C, respectively. Moreover, 2,2′-disubstituted-1,1′-binaphthyls and, to a lesser extent 2,2′-disubstituted-6,6′-dimethyl-1,1′-biphenyls, are of interest as chiral auxiliaries in the area of asymmetric synthesis.[12]

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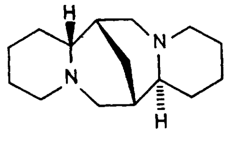
† 2,2′-Bis[(*N,N,N′,N′*-tetramethylethylenediamine)lithiomethyl]-1,1′-binaphthyl and 2,2′,6-trimethyl-6′-[(*N,N,N′,N′,N″*-pentamethyldiethylenetriamine)lithiomethyl]-1,1′-biphenyl.

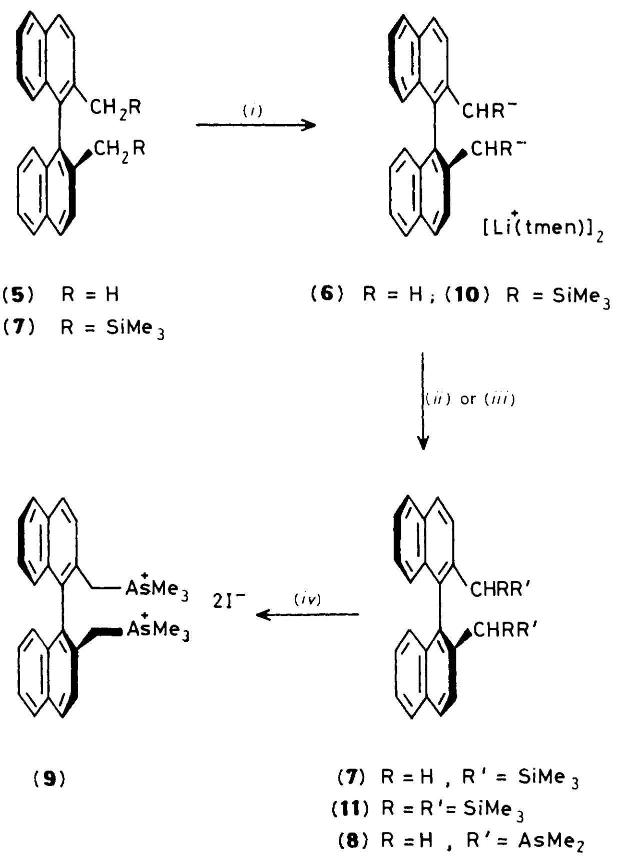
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: 1 mmHg ≈ 133 Pa.



(4)

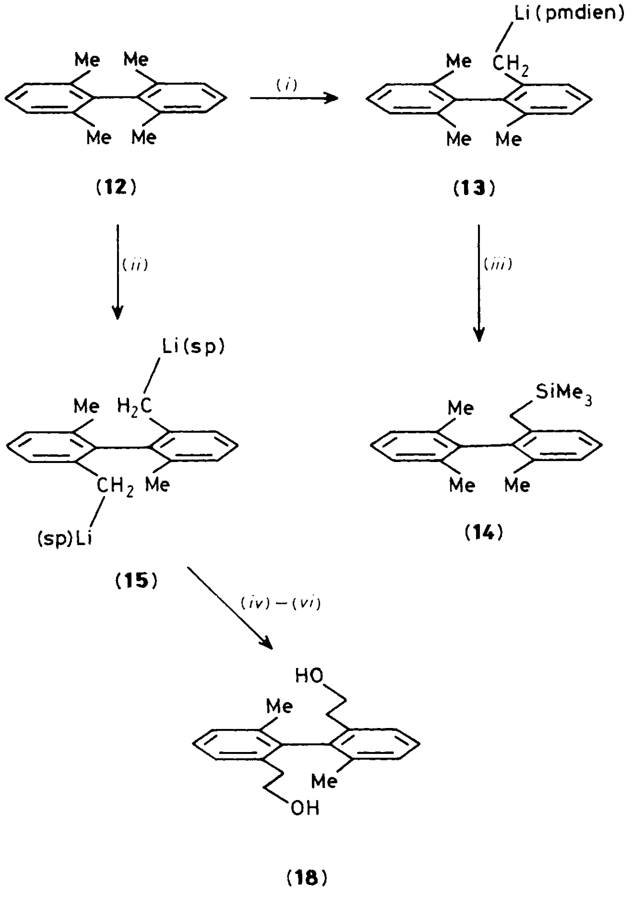
Metallation using LiBu^n in the presence of a tertiary amine, tmen, pmdien (pmdien = *N,N,N′,N′N″*-pentamethyldiethylenetriamine) or (−)sparteine, (**4**),[13] features in the present study. Both tmen and pmdien have been used extensively for the lithiation of arylmethanes.[14] The use of (−)sparteine for the same purpose is restricted to the asymmetric dilithiation, albeit in 3% optical yield, of a mono-substituted ferrocene.[15]



Scheme 1. (*i*) 2 LiBu^n(tmen) in Et$_2$O (R = H) or hexane (R = SiMe$_3$); (*ii*) excess of SiMe$_3$Cl, thf; (*iii*) excess of AsMe$_2$I, thf; (*iv*) excess of MeI, hexane

Results and Discussion

Metallation of 2,2′-dimethyl-1,1′-binaphthyl, (**5**), its α,α′-bis(trimethylsilyl) derivative, (**7**), and 2,2′,6,6′-tetramethyl-1,1′-biphenyl, (**12**), yielded the α-lithioarylmethane species shown in Schemes 1 and 2. These were characterised by ^{1}H and ^{13}C n.m.r. spectroscopy, and for compounds (**6**) and (**13**) crystal-structure determinations were performed. The site(s) of metallation have been clarified by reactions with SiMe$_3$Cl or CO$_2$.



Scheme 2. (*i*) LiBu^n(pmdien), Et$_2$O; (*ii*) 2 LiBu^n(sp), Et$_2$O; (*iii*) SiMe$_3$Cl, hexane; (*iv*) CO$_2$, hexane, −78 °C; (*v*) CH$_2$N$_2$, Et$_2$O, 0 °C; (*vi*) LiAlH$_4$, Et$_2$O. sp = (−)Sparteine

Binaphthyl Chemistry.—Metallation of both (**5**) and (**7**) using LiBu^n(tmen) gave crystalline dilithio species in modest yield, a result consistent with facile dimetallation of the corresponding compounds based on biphenyl, *viz.* (o-RCH$_2$C$_6$H$_4$)$_2$, R = H or SiMe$_3$.[2] Both the binaphthyl and biphenyl systems have the metallation sites on independent rings, across which conjugation is blocked because of a large dihedral angle between them; dimetallation of compounds bearing methyl groups attached to the same aromatic ring fails using LiBu^n(tmen),[13,16–19] unlike when the methyl groups bear –SiMe$_3$ substituents.[2,13,17–20]

The previous dimetallation of (**5**) involved using excess of LiBu^n(tmen) in hexane (*cf.* Et$_2$O in the present study) and the product was subsequently used *in situ*.[7] We find that lithium reagents of this type are best isolated, and even recrystallized, prior to use.[21] Treating compound (**6**) with SiMe$_3$Cl in thf yielded (**7**). It is of interest to compare this with the reaction of mono-lithiated 2,3-dimethylnaphthalene[22] and 9-methyl- or 9-(trimethylsilyl)anthracene[23,24] with SiMe$_3$Cl, which yield ring-silylated species. For the former, a silyl group becomes attached to the 1-position. This position is substituted in (**5**) which would favour silylation of the benzylic carbon centres. Compound (**6**) also reacts with AsMe$_2$I to afford the benzylic substituted derivative, (**8**), although it could not be purified by distillation, because of decomposition, or recrystallization. Addition of MeI, however, gave the quaternary arsonium salt, (**9**), as analytically pure, crystalline material. Quenching compound (**10**) with SiMe$_3$Cl gave the tetrakis compound, (**11**).

Biphenyl Chemistry.—Attempts selectively to dilithiate 2,2′,6,6′-tetramethylbiphenyl, (**12**), using two equivalents of LiBu^n(tmen) in hexane or diethyl ether, failed. Gas chromatography–mass spectroscopy (g.c.–m.s.) of $SiMe_3Cl$-quenched reaction mixtures showed a mixture of products ranging from starting material through to a tetrakis(trimethylsilyl) derivative (ratio *ca.* 3 : 1 : 1 : 8 : 6). This result is related to the lack of selective monolithiation of *m*-xylene using the same reagent.[18] Predominantly, dimetallation, of unknown specificity, or tetrametallation of isomeric 3,3′,5,5′-tetramethyl-1,1′-biphenyl is possible using $LiBu^n$(tmen)–K(OBu^t).[25] (The tetra-anion of 3,3′,5,5′-tetramethyl-1,1′-biphenyl can also be generated *via* a metallation–metal hydride elimination procedure.[25]) In general, the metallation of two methyl groups attached to the same aromatic ring system requires mixed $LiBu^n$–K(OR) (R = alkyl) reagents[17,26,27] or Na(tmen)(n-C_5H_{11}).[28]

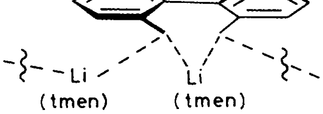
Compound (**12**), with two equivalents of $LiBu^n$(pmdien) in hexane afforded a crystalline material which was shown by g.c.–m.s. of a $SiMe_3Cl$-quenched mixture to contain both the mono- and di-lithiated species in 37 and 57% yield respectively, and a trace of the trilithiated compound. Treatment of (**12**) with one equivalent of the metallating reagent in diethyl ether, however, afforded the mono-lithiated compound in almost quantitative yield, isolated as a crystalline solid, (**13**), which has been structurally authenticated (see below) and its trimethylsilyl derivative, (**14**), prepared. Thus selective dimetallation using tmen or pmdien tertiary amines with $LiBu^n$ is elusive whereas selective mono-metallation is possible using $LiBu^n$(pmdien). The potential of this reagent as a highly selective and reactive metallating reagent, under certain conditions, is gradually being realised.[13,17,28,29]

Reaction of (**12**) with $LiBu^n$(sp) in diethyl ether gave the dimetallated species (**15**), isolated as a solid in high yield and characterized by n.m.r. spectroscopy and formation of a dicarboxylic acid (**16**). The success of this reagent over $LiBu^n$(tmen) or $LiBu^n$(pmdien) for dimetallation is surprising. Methyl groups attached to different aromatic rings, rather than to the same ring, are metallated in accordance with reduced acidity of a methyl group attached to a ring already stabilizing charge by delocalization. Dimetallation produces a chiral dianion, thus if optically active sparteine can relay asymmetry, either during metallation, *i.e.* asymmetric or enantioselective metallation, and/or subsequent inter- or intra-H–Li exchange, one diastereoisomer of (**15**) may be preferred. In testing this, (**15**) was carboxylated at −78 °C and the derived diacid, (**16**), converted to a dimethyl ester, (**17**), and reduced to the corresponding diol, (**18**) (Scheme 2). An enantiomeric excess of 40% was then established using a ^1H n.m.r. spectroscopy–lanthanide shift reagent technique. Optimum separation of peaks was achieved for 0.36 mol equivalent of tris[3-(perfluorobutyryl)bornan-2-onato]europium(III) at a concentration for (**18**) of *ca.* 0.1 g cm^{-3} in $CDCl_3$.

Thus there is modest asymmetric induction, significantly more than was established for a similar reaction of a substituted ferrocene.[15]

Structural Commentary.—The structure determinations of (**6**) and (**13**) establish the solids to comprise discrete monomers of (**6**) and (**13**). Results are shown in Tables 1—4, and Figures 1 and 2 which define the numbering schemes. The asymmetric unit in each is one complete molecule.

The lithium environments in (**6**) are different with respect to the hydrocarbyl group interaction; Li(B) bridges the *ipso* carbons, C(A1) [2.13(5)] and C(B1) [2.23(5) Å], thus forming a metallacycle, and Li(A) is η^2-bound to one of the *ipso* carbons, C(A1), and its nearest neighbour, at 2.36(5) and 2.51(5) Å, respectively, on the opposite side of the naphthalene plane to Li(B). The $[Li(tmen)]^+$ entities strongly resemble those in other organolithium species, for example in $[\{Li(tmen)\}_2\{(o\text{-}CH_2C_6H_4)_2\}]$, (**19**),[2] which differ from the structure of (**6**) in



(**19**)

Table 1. Non-hydrogen atom parameters for compound (**6**)

Ligand/Section	A				B			
Atom	*x*	*y*	*z*	$10^3U/Å^2$	*x*	*y*	*z*	$10^3U/Å^2$
Li	0.153(1)	0.469(4)	−0.111(2)	70(13)	0.088(1)	0.685(4)	−0.011(2)	65(13)
Binaphthyl ligand								
C(1)	0.128 3(6)	0.692(2)	−0.058 5(9)	51(6)	0.069 0(6)	0.512(2)	0.031 0(10)	67(7)
C(2)	0.157 6(6)	0.561(2)	0.003 7(9)	50(6)	0.073 9(6)	0.422(2)	−0.016 9(10)	58(7)
C(3)	0.200 7(6)	0.617(2)	0.050 3(10)	65(7)	0.032 1(6)	0.375(2)	−0.076 0(10)	62(7)
C(4)	0.229 1(6)	0.560(2)	0.110 9(10)	67(7)	0.031 5(6)	0.285(2)	−0.124 2(10)	70(7)
C(5)	0.219 9(6)	0.446(2)	0.135 8(9)	52(7)	0.066 1(6)	0.236(2)	−0.123 9(9)	48(6)
C(6)	0.178 7(6)	0.390(2)	0.093 8(9)	45(6)	0.106 7(6)	0.283(2)	−0.069 4(9)	48(6)
C(7)	0.149 5(6)	0.439(2)	0.025 4(9)	40(6)	0.109 0(5)	0.381(2)	−0.020 9(9)	37(6)
C(8)	0.170 3(6)	0.276(2)	0.119 6(10)	55(7)	0.143 2(6)	0.233(2)	−0.071 7(10)	58(7)
C(9)	0.198 1(6)	0.221(2)	0.185 1(10)	73(8)	0.144 2(7)	0.133(2)	−0.118 9(11)	87(8)
C(10)	0.238 5(6)	0.285(2)	0.225 2(9)	53(7)	0.102 3(7)	0.093(2)	−0.170 1(11)	79(8)
C(11)	0.249 2(6)	0.391(2)	0.202 8(10)	57(7)	0.066 1(6)	0.136(2)	−0.170 4(10)	75(8)
tmen ligand								
N(1)	0.209 1(5)	0.472(2)	−0.115 9(9)	132(7)	0.029 0(5)	0.797(2)	−0.080 5(8)	113(6)
C(1)	0.195 5(8)	0.442(2)	−0.193 0(13)	130(11)	0.040 6(8)	0.934(2)	−0.050 4(13)	129(11)
C(11)	0.237 6(7)	0.366(2)	−0.076 4(11)	84(8)	0.026 4(8)	0.799(3)	−0.153 7(13)	128(11)
C(12)	0.229 5(9)	0.593(3)	−0.092 9(14)	155(12)	−0.009 8(8)	0.756(3)	−0.073 6(13)	121(10)
N(2)	0.120 5(5)	0.501(2)	−0.224 7(9)	147(7)	0.109 0(6)	0.868(2)	0.054 1(10)	160(8)
C(2)	0.157 5(8)	0.500(3)	−0.238 3(13)	132(10)	0.069 5(11)	0.945(3)	0.016 6(19)	222(16)
C(21)	0.090 3(8)	0.403(3)	−0.260 5(14)	134(11)	0.115 4(11)	0.848(3)	0.132 6(19)	216(15)
C(22)	0.104 7(9)	0.637(3)	−0.249 4(15)	170(13)	0.144 7(10)	0.913(3)	0.050 0(16)	175(13)

Table 2. Non-hydrogen atom co-ordinates for compound (**13**)

	Section A			Section B		
Atom	x	y	z	x	y	z
Li	0.694 4(8)	0.137 7(11)	−0.270 8(18)			
Biphenyl ligand						
C(1)	0.666 8(5)	0.269 0(6)	−0.216 0(12)	0.514 8(6)	0.419 1(7)	−0.200 7(14)
C(2)	0.654 2(7)	0.298 2(6)	−0.064 4(13)	0.493 2(7)	0.326 3(9)	−0.195 3(16)
C(3)	0.711 1(6)	0.324 4(7)	0.034 6(17)	0.437 8(7)	0.294 3(11)	−0.286 5(16)
C(4)	0.701 8(7)	0.348 4(8)	0.183 6(20)	0.416 6(6)	0.209 7(13)	−0.279 4(16)
C(5)	0.640 4(9)	0.351 0(8)	0.250 8(13)	0.451 0(8)	0.152 8(8)	−0.179 2(16)
C(6)	0.582 2(7)	0.325 4(7)	0.161 9(16)	0.508 1(6)	0.182 5(9)	−0.089 4(13)
C(61)	0.511 1(6)	0.323 1(8)	0.222 8(13)	0.545 5(6)	0.119 6(7)	0.015 2(13)
C(7)	0.589 0(6)	0.300 1(6)	0.010 2(17)	0.528 4(6)	0.269 6(9)	−0.092 2(13)
pmdien Ligand						
N(1)	0.753 5(5)	0.055 8(7)	−0.119 6(11)	0.633 6(5)	0.073 7(8)	−0.447 8(11)
C(10)	0.763 2(6)	0.098 1(7)	0.027 3(14)	0.586 4(7)	0.137 7(8)	−0.513 2(13)
C(11)	0.731 5(9)	−0.032 3(9)	−0.100 4(18)	0.595 4(8)	−0.002 5(9)	−0.404 1(18)
C(12)	0.820 3(9)	0.060 1(14)	−0.189 8(18)	0.684 0(10)	0.046 2(14)	−0.553 6(20)
C(21)	0.823 2(7)	0.069 5(9)	−0.343 9(20)	0.744 4(10)	0.097 5(11)	−0.564 8(19)
N(2)	0.776 6(5)	0.130 4(8)	−0.421 5(13)			
C(20)	0.812 7(6)	0.212 3(10)	−0.451 8(15)			

Table 3. Lithium environments in compound (**6**). Distances in Å, angles in °

Li(A)–N(A1)	2.00(5)	Li(B)–N(B1)	2.24(4)
Li(A)–N(A2)	2.12(4)	Li(B)–N(B2)	2.25(4)
Li(A)–C(A1)	2.36(5)	Li(B)–C(A1)	2.13(5)
Li(A)–C(A2)	2.51(5)	Li(B)–C(B1)	2.23(5)
N(A1)–Li(A)–N(A2)	90(2)	N(B1)–Li(B)–N(B2)	84(1)
N(A1)–Li(A)–C(A1)	126(2)	N(B1)–Li(B)–C(A1)	117(2)
N(A1)–Li(A)–C(A2)	114(2)	N(B2)–Li(B)–C(A1)	114(2)
N(A2)–Li(A)–C(A1)	106(2)	N(B1)–Li(B)–C(B1)	109(2)
N(A2)–Li(A)–C(A2)	140(2)	N(B2)–Li(B)–C(B1)	122(2)
C(1A)–Li(A)–C(A2)	34(1)	C(A1)–Li(B)–C(B1)	109(2)

Table 4. Lithium environment for compound (**13**). Distances in Å, angles in °

Li–N(1A)	2.11(2)	Li–N(2)	2.12(2)
Li–N(1B)	2.13(2)	Li–C(1A)	2.14(2)
N(1A)–Li–N(1B)	116.5(9)	N(1B)–Li–N(2)	86.2(7)
N(1A)–Li–N(2)	87.4(7)	N(1B)–Li–C(1A)	117.1(8)
N(1A)–Li–C(1A)	123.4(8)	N(2)–Li–C(1A)	113.1(8)

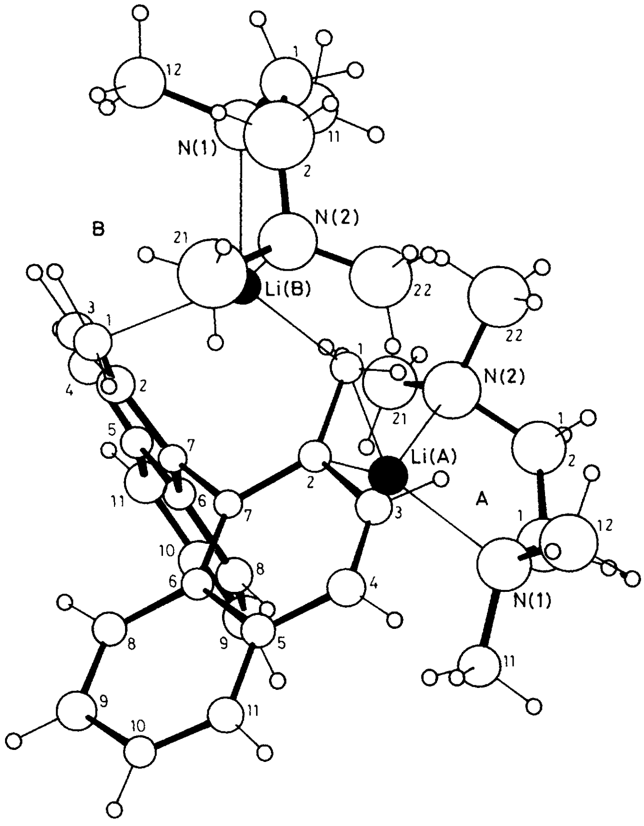


Figure 1. Molecular projections of [{Li(tmen)}$_2${(2-CH$_2$C$_{10}$H$_6$)$_2$}], (**6**); all atoms have arbitrary radii

that the lithium, which is not part of the metallacycle, bridges successive anions yielding a polymeric structure, and has an environment like Li(B). In benzene, (**19**) is dimeric, presumably with lithium to hydrocarbyl interactions similar to those in the solid.

The difference in the structures of (**6**) and (**19**) may be a consequence of the greater steric requirements of the naphthyl groups in (**6**), restricting close approach of the dianions, (**3**), R = H. The Li–N distances are unexceptional and the Li–C distances are within the range established for related structures.[2,14]

The *ipso*-carbon, C(A1), appears to be trigonal planar with contacts to two metal centres; the angle subtended by the two lithium centres is 150(2)° which compares with 163(1)° for the corresponding carbon in compound (**19**).[2] Metal centres bridged by such trigonal-planar carbon centres have recently appeared in the literature for lithium[2,30] and zirconium[31] and have been discussed theoretically.[31–33] They model the transition state of transmetallation reactions that proceed with inversion at carbon.[31]

The distinction between the lithium centres in the solid of (**6**) is seemingly maintained in toluene solution on the ^{7}Li n.m.r. time-scale below *ca.* −28 °C. A single ^{7}Li resonance collapsed with the appearance of two singlets, $E_{act.}$ 46 ± 1 kJ mol^{-1}.

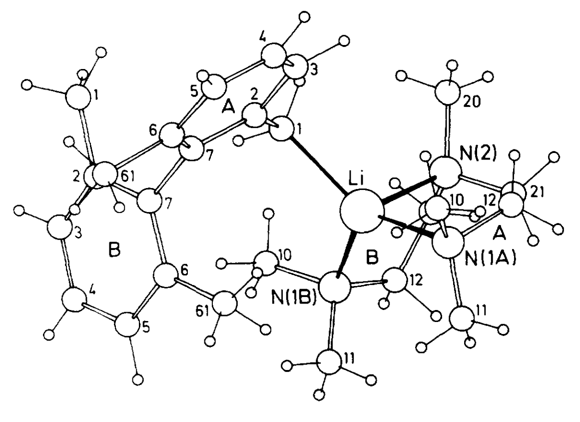


Figure 2. Molecular projection of $[\{Li(pmdien)\}\{2\text{-}CH_2\text{-}6\text{-}Me(C_6H_3)_2\text{-}2',6'\text{-}Me_2\}]$, (**13**); all atoms have arbitrary radii

In (**13**) the metal has four-fold co-ordination with only one contact to the hydrocarbyl group which is prevalent when three neutral donor groups are attached to lithium, *e.g.* in [Li(pmdien)R], R = $CH(SiMe_3)_2$,[34] *o*-$SiMe_3CHC_6H_4Me$,[35] Ph,[36] $[\{Li(tmen)(CH_2PMe_2)\}_2]$,[37] and $[\{Li(tmen)(CH_2SPh)\}_2]$ and related systems.[38] The Li–C distance in (**13**), 2.14(2) Å, compares with the range 2.13(5)[34]—2.26(1) Å[35] found in these types of compounds. The only exception to interaction with one carbon centre is $[\{Li(pmdien)\}_2(PhCH{=}CHPh)]$ where the lithium atoms are η^2-bound to the olefinic bond.[39] The Li–N distances, 2.11(2)—2.13(2) Å, are comparable with those found in the Li–pmdien complex with ferrocene, 2.115(9)—2.162(9) Å,[40] and [Li(pmdien)Ph], 2.13—2.15 Å,[36] but shorter than those found in the derivative of the stilbene dianion, 2.165(6), 2.189(6) Å,[39] and $[\{Li(pmdien)\}\{CH(SiMe_3)_2\}]$, 2.20(4)—2.30(4) Å.[34] The chiralities of the two ethylene linkages in pmdien are the same (N–C–C–N torsion angles both 42°).

The dihedral angle between the two naphthyl systems in (**6**) is 82.0°. This is controlled to some extent by the size of the atom bridging the *ipso* carbons:[6] the larger the metal the larger the angle. This is illustrated by the silicon heterocycle based on (**2**), R = H, having a lower dihedral angle 65.5°.[41] In (**13**) the aromatic rings are not restricted by a bridging metal centre and the angle is enlarged to 84.7°. The aromatic ring skeleton and attached carbon atoms are closely planar in both structures. In (**6**) Li(A) resides 2.12 and 2.46 Å out of the planes for section A and B, respectively. Corresponding values for Li(B) are −2.21 and 1.94 Å. The Li atom in (**13**) is 1.90 Å out of its associated aromatic plane. As expected from delocalization of charge the *ipso*-carbon to ring-carbon distances are shortened by *ca.* 0.05 Å relative to the C_{aryl}–CH_3 distances [C(1)–C(2) in (**6**), 1.42(2), 1.43(2) Å, for sections A and B respectively, and in (**13**), 1.43(2) Å].

Experimental

General Procedure.—The procedures used are described in Parts 1,[2] 2,[3] and 3[5] of this series.

Synthesis of 2,2′-*Dimethyl*-1,1′-*binaphthyl*, (**5**).—A yellow viscous oil of compound (**5**) was prepared by the method of Bestmann and Both.[42] This was crystallized by freezing the oil at −196 °C, pulverizing the resulting solid, then adding acetone [*ca.* 5 cm^3 for 50 g of (**5**)] and storing the mixture overnight at −30 °C. The resulting white prisms were collected and recrystallized from the minimum quantity of acetone.

Synthesis of $[\{Li(tmen)\}_2\{(2\text{-}CH_2C_{10}H_6)_2\}]$, (**6**).—A solution of LiBu^n in hexane (35 cm^3, 1.7 mol dm^{-3}, 60 mmol) was concentrated *in vacuo* and the residual oil dissolved in diethyl ether (35 cm^3). After cooling the solution to 0 °C solid 2,2′-dimethyl-1,1′-binaphthyl (7.0 g, 25 mmol) was added with stirring to give a red solution. Tmen (9.1 cm^3, 61 mmol) was added slowly after which the resulting solution was kept for 12 h at room temperature, yielding deep red prisms. These were collected, washed with pentane (3 × *ca.* 5 cm^3), and dried *in vacuo* (7.8 g, 60%). M.p. 158—160 °C. ^{1}H N.m.r. (C_6D_6); δ 1.98 [m, 36 H, 2 CH_2 (aryl), 4 CH_2N, 8 NMe], 6.80—8.30 (m, 12 H, $C_{10}H_6$). ^{13}C-{^{1}H} N.m.r. (C_6D_6); δ 43.1 [2 CH_2 (aryl)], 45.7 (8 NMe), 57.1 (4 CH_2N), 108.9—150.2 ($2C_{10}H_6$). ^{7}Li N.m.r. (toluene, relative to external aqueous $LiNO_3$); δ 0.12 (s), 30 °C; 1.38, −1.11 (s), −80 °C.

Synthesis of 2,2′-*Bis*(*trimethylsilylmethyl*)-1,1′-*binaphthyl*, (**7**).—Compound (**6**) (4.50 g, 8.5 mmol) was dissolved in thf (60 cm^3) and excess of $SiMe_3Cl$ (2.5 cm^3, 20.5 mmol) added with stirring at room temperature. The mixture was then stirred for 12 h. After removing the solvent *in vacuo* CH_2Cl_2 (70 cm^3) and dilute HCl (30 cm^3, 2 mol dm^{-3}) were added. The organic layer was separated and the aqueous layer washed with more CH_2Cl_2 (3 × 20 cm^3). The combined organic washings were shaken with water (50 cm^3) then dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* gave a white solid of (**7**) which was recrystallized from acetone (*ca.* 20 cm^3) as colourless prisms (2.33 g, 64%). M.p. 78—79 °C (Found: C, 78.7; H, 8.15. Calc. for $C_{28}H_{34}Si_2$: C, 78.7; H, 8.00%). ^{1}H N.m.r. ($CDCl_3$); δ −0.32 (s, 18 H, SiMe), 2.27 (s, 4 H, CH_2), 6.92—7.90 (m, 12 H, $C_{10}H_6$). Mass spectrum, *m/e* 427 (P^+), 323, 73.

Synthesis of 2,2′-*Bis*(*dimethylarsinomethyl*)-1,1′-*binaphthyl*, (**8**).—The organodilithium reagent, (**6**) (5.2 g, 9.9 mmol) was dissolved in thf (60 cm^3) and $AsMe_2I$ (0.73 cm^3, 10 mmol) added dropwise with stirring at room temperature. On completion of the addition the solvent was removed *in vacuo* and deoxygenated diethyl ether (50 cm^3) and concentrated HCl (50 cm^3) added. The ethereal layer was separated and the aqueous layer further extracted with diethyl ether (20 cm^3). The combined extracts were washed with water, dried, filtered, and then concentrated *in vacuo*. The residue was placed under vacuum (*ca.* 10^{-2} mmHg) for 6 h to remove any tmen or unreacted $AsMe_2I$. Yield of crude (**8**), 4.3 g, 90%. ^{1}H N.m.r. ($CDCl_3$); δ 0.37 (s, 6 H, AsMe), 0.60 (s, 6 H, AsMe), 2.43 (s, 4 H, CH_2), 6.80—7.80 (m, 12 H, $C_{10}H_6$).

Synthesis of 2,2′-*Bis*(*trimethylarsoniomethyl*)-1,1′-*binaphthyl Iodide*, (**9**).—The diarsine (**8**) (4.3 g, 8.8 mmol) was dissolved in MeI (5 cm^3). Hexane (20 cm^3) was then slowly added to give a yellow-brown oil. After removal of the solvent *in vacuo* the residue was taken up in acetone (20 cm^3) then cooled to −30 °C whereupon a pale yellow powder formed. This was collected and recrystallized from hot methanol yielding pale yellow needles of (**9**) (4.2 g, 60%). M.p. >260 °C (Found: C, 43.4; H, 4.55. Calc. for $C_{28}H_{34}As_2I_2$: C, 43.4; H, 4.40%). ^{1}H N.m.r. [$(CD_3)_2SO$]; δ 1.40 (s, 18 H, AsMe), 3.67 (AB quartet, J_{H-H} 14 Hz, 4 H, CH_2), 6.73—8.27 (m, 12 H, $C_{10}H_6$).

Synthesis of $[\{Li(tmen)\}_2\{(2\text{-}Me_3SiCHC_{10}H_6)_2\}]$, (**10**).—To a cooled solution of LiBu^n in hexane (5.9 cm^3, 1.6 mol dm^{-3}, 9.4 mmol) was added 2,2′-bis(trimethylsilylmethyl)-1,1′-binaphthyl, (**7**) (1.0 g, 2.3 mmol) and tmen (1.54 cm^3, 10.3 mmol) with stirring. The solution was then kept at −30 °C overnight during which red-brown needles of (**10**) formed. These were collected and washed with pentane (3 × 5 cm^3) then dried *in vacuo* (1.1 g, 66%). M.p. 130—132 °C. ^{1}H N.m.r. (C_6D_6); δ 0.47 (s, 18 H, 2 $SiMe_3$), 1.77 (m, 32 H, 4 CH_2N, 8 NMe), 2.15 (s, 2 H, 2 CH), 6.57—7.60 (m, 12 H, $C_{10}H_6$). ^{13}C-{^{1}H} N.m.r. (C_6D_6); δ 3.3 (2 SiMe), 53.8 (2 CH), 56.8 (4 CH_2N), 109.3—151.8 (2 $C_{10}H_6$).

Synthesis of 2,2′-Bis[bis(trimethylsilyl)methyl]-1,1′-binaphthyl, (**11**).—This was prepared as for compound (**7**) using the diorganodilithium reagent (**10**) (1.0 g, 1.5 mmol), being crystallized from acetone as colourless prisms (0.5 g, 58%). M.p. 160—162 °C (Found: C, 71.0; H, 8.90. Calc. for $C_{34}H_{50}Si_4$: C, 71.4; H, 8.80%). ^{1}H N.m.r. ($CDCl_3$); δ −0.35 (s, 18 H, 2 $SiMe_3$), 0.28 (s, 18 H, 2 $SiMe_3$), 2.07 (s, 2 H, 2 CH), 6.37—7.92 (m, 12 H, $C_{10}H_6$). Mass spectrum, *m/e*: 571 (P^+), 556, 483, 468, and 395.

Synthesis of [{Li(pmdien)}{2-CH_2-6-Me(C_6H_3)$_2$-2′,6′-Me_2}], (**13**).—To an ice-cooled solution of 2,2′,6,6′-tetramethyl-1,1′-biphenyl, (**12**) (0.6 g, 2.86 mmol) in diethyl ether (2 cm^3) and LiBu^n in n-hexane (2.0 cm^3, 1.60 mol dm^{-3}, 3.1 mmol) was added pmdien (0.55 g, 3.10 mmol). The resulting light yellow solution was kept at room temperature for 18 h during which yellow crystals of (**13**) formed. These were filtered off, washed with cold (*ca.* −20 °C) pentane (2 × 3 cm^3), and dried *in vacuo* (1.1 g, 98.9%). M.p. 119—120 °C. ^{1}H N.m.r. (C_6D_6); δ 1.50 (s, 2 H, CH_2), 1.76 and 1.80 (s, 8 H, 4 NCH_2), 1.87 (s, 12 H, 4 NMe), 1.96 (s, 3 H, NMe), 2.03 (s, 6 H, 2 Me), 2.40 (s, 3 H, Me), 6.2—7.0 (m, 6 H, C_6H_3). ^{13}C-{^{1}H} N.m.r. (C_6D_6); δ 20.4 [2 CH_3 (aryl)], 20.9 [CH_3 (aryl)], 35.0 ($LiCH_2$), 44.5 (4 NMe), 46.6 (NMe), 53.2, 53.5 (4 NCH_2), 109.2—157.8 (2 C_6H_3). ^{7}Li N.m.r. (toluene); δ 0.46 (30 °C).

Synthesis of 2,2′,6-Trimethyl-6′-trimethylsilylmethyl-1,1′-biphenyl, (**14**).—To a stirred suspension of the organolithium reagent (**13**) (5.2 g, 15 mmol) in hexane (20 cm^3) at 0 °C was slowly added $SiMe_3Cl$ (1.8 g, 17.5 mmol). After stirring at room temperature for 1 h excess of $SiMe_3Cl$ and hexane were removed *in vacuo* then dilute HCl added (20 cm^3, 2 mol dm^{-3}). The residue was taken up in hexane (30 cm^3) and distilled yielding (**14**) as a colourless liquid (2.6 g, 61%). B.p. 78 °C (0.2 mmHg). ^{1}H N.m.r. ($CDCl_3$); δ −0.63 (s, 9 H, $SiMe_3$), 1.79 (s, 2 H, CH_2), 1.92 (s, 6 H, 2 Me), 1.95 (s, 3 H, Me), 7.1 (m, 6 H, C_6H_3). ^{13}C-{^{1}H} N.m.r. ($CDCl_3$); δ −0.2 (SiMe), 20.4 [2 Me (aryl)], 20.5 [Me (aryl)], 22.8 (CH_2), 116.4—152.4 (C_6H_3). Mass spectrum, *m/e*: 282 (P^+), 267, 252, 237, and 209.

Synthesis of [{Li(sp)}$_2${(2-CH_2-6-MeC_6H_3)$_2$}], (**15**).—Hexane was removed *in vacuo* from a solution of LiBu^n in hexane (12.1 cm^3, 1.7 mol dm^{-3}, 20.5 mmol) and the residual oil dissolved in diethyl ether (30 cm^3). 2,2′,6,6′-Tetramethyl-1,1′-biphenyl (2.0 g, 9.5 mmol) was dissolved in the solution which was then cooled to 0 °C and (−)sparteine (4.8 cm^3, 20.9 mmol) added dropwise with stirring. The resulting solution was then left at 20 °C for 12 h yielding a yellow solid. This was washed with cold pentane (3 × *ca.* 5 cm^3) and dried *in vacuo* (5.7 g, 87%). M.p. 69 °C (decomp.). ^{1}H N.m.r. (C_6D_6); δ 0.91—3.31 [m, 62 H, CH_2 (aryl), CH_3 (−)sparteine], 6.21—6.29 [m, 2 H, CH(aryl)], 6.63—7.16 [m, 4 H, CH(aryl)]. ^{13}C-{^{1}H} N.m.r. (C_6D_6); δ 21.0 (CH_3), 35.3 [CH_2 (aryl)], 20.4, 24.9, 28.5, 29.9, 35.3, 46.0, 53.6, 58.3, 59.1, 61.8, 67.4 [(−)sparteine], 110.3, 116.9, 126.0, 130.1, 133.9, and 154.6 (C_6H_3). ^{7}Li N.m.r. (toluene); δ 0.16 (30 °C).

Synthesis of 6,6′-Dimethyl-2,2′-biphenyldiethanoic Acid, (**16**).—Finely crushed CO_2 (10 g, 0.23 mol) was added to a stirred hexane solution (20 cm^3) of (**15**) (2.2 g, 3.1 mmol) at −78 °C. The temperature was raised to *ca.* 20 °C over 1 h whereupon 6 mol dm^{-3} HCl (10 cm^3) was added and the mixture stirred overnight. Volatiles were removed *in vacuo* and the residue extracted with CH_2Cl_2 (3 × 10 cm^3) and washed with NaOH (25 cm^3, 1 mol dm^{-3}). The aqueous layer was then acidified with HCl (10 cm^3, 6 mol dm^{-3}) and extracted with CH_2Cl_2 (3 × 10 cm^3), dried over $MgSO_4$, filtered, and taken to dryness *in vacuo*. The resulting white solid, (**16**), was recrystallized from acetone (0.8 g, 80%). M.p. 176—177 °C (Found: C, 72.7; H, 6.00. Calc. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.10%). ^{1}H N.m.r. ($CDCl_3$); δ 1.80 (s, 6 H, CH_3), 3.30 (s, 4 H, CH_2), 7.17 [m, 6 H, CH(aryl)], 11.0 (s, 2 H, OH, exchanges with D_2O). ^{13}C-{^{1}H} N.m.r. ($CDCl_3$); δ 20.1 (CH_3), 37.4 (CH_2), 127.6, 128.8, 129.2 [CH(aryl)], 131.9, 136.2, 139.1 [C(aryl)], 179.1 (CO). Mass spectrum, *m/e* 298 (P^+), 280, 207, 193, and 178; $[\alpha]_D$ = 6.3°, $[\alpha]_{Hg\,436}$ = 11.9° (*c* = 13 mol dm^{-3}, diethyl ether).

Synthesis of Dimethyl 6,6′-Dimethyl-2,2′-biphenyldiethanoate, (**17**).—Freshly distilled diazomethane was added cautiously to (**16**) (0.21 g, 0.7 mmol) in diethyl ether at 0 °C until the colourless solution turned yellow. After 15 min the mixture was warmed until the yellow colour disappeared. Solvent was then removed *in vacuo* and (**17**) distilled as a colourless oil, 140—142 °C (0.1 mmHg) (0.22 g, 96%). ^{1}H N.m.r. ($CDCl_3$); δ 1.77 [s, 6 H, CH_3(aryl)], 2.89 (s, 4 H, CH_2), 3.39 (s, 6 H, OCH_3), 7.07 (m, 6 H, C_6H_3). ^{13}C-{^{1}H} N.m.r. ($CDCl_3$); δ 19.6 [CH_3(aryl)], 38.0 (CH_2), 51.3 (CH_3), 127.5 [2 CH(aryl)], 128.8 [CH(aryl)], 132.3, 136.3, 138.7 [C(aryl)], 171.7 (CO). Mass spectrum *m/e*: 326 (P^+), 294, 207, 193, 178; α_{589} = −12.4°, α_{436} = −25.3° (*c* = 29 mol dm^{-3}, diethyl ether).

Synthesis of 2,2′-Bis(β-hydroxyethyl)-6,6′-dimethyl-1,1′-biphenyl, (**18**).—A mixture of (**17**) (0.2 g, 0.7 mmol), $LiAlH_4$ (0.2 g, 5.9 mmol), and diethyl ether (50 cm^3) was refluxed for 12 h. On cooling to 0 °C, water (2 cm^3) and 15% NaOH solution (2 cm^3) were slowly added, the diethyl ether layer separated and dried over $MgSO_4$, and concentrated *in vacuo*. Compound (**18**) was distilled, 150—152 °C (0.1 mmHg) as a colourless liquid (0.2 g, 95%) (Found: C, 79.8; H, 8.15. Calc. for $C_{18}H_{22}O_2$: C, 80.0; H, 8.20%). ^{1}H N.m.r. ($CDCl_3$); δ 1.90 (s, 6 H, CH_3), 2.42 [t, 4 H, CH_2(aryl), *J* = 7 Hz], 2.52 (s, 1 H, OH, exchanges with D_2O), 3.57 (t, 4 H, CH_2O, *J* = 7 Hz), 7.12 (m, 6 H, C_6H_3). ^{13}C-{^{1}H} N.m.r. ($CDCl_3$); δ 20.0 (CH_3), 35.9 [CH_2(aryl)], 61.9 (CH_2O), 126.5, 127.3, 128.3 [CH(aryl)], 136.1, 136.4, 139.6[C(aryl)]. Mass spectrum, *m/e*: 252 (P–H_2O^+), 223, 209, 207, 206, 195, 193, 192, 191, and 179; α_{589} = −9.2°, α_{436} = −20.1° (*c* = 31 mol dm^{-3}, diethyl ether).

Structure Determinations.—Unique data sets were measured at *ca.* 295 K on specimens mounted in capillaries within the limit $2\theta_{max.}$ = 40° using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ–θ scan mode and fitted with a monochromatic Mo-K_α radiation source (λ = 0.7106$_9$ Å). *N* Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the block-diagonal least-squares refinement without absorption correction after solution of the structure by direct methods. For compound (**13**), anisotropic thermal parameters were refined for the non-hydrogen atoms; for compound (**6**), there were insufficient data to support this and the isotropic form was used. All *x*, *y*, *z*, and U_{iso}(H) were included in both cases as constrained estimates. Residuals on |*F*| at convergence *R*, *R′* are quoted. Neutral atom complex scattering factors were used;[43] computation used the XTAL program system[44] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Non-hydrogen atom numberings are shown in Figures 1 and 2 and atomic co-ordinates and relevant bond lengths and angles are given in Tables 1—4.

Crystal data. (**6**). $C_{34}H_{48}Li_2N_4$, *M* = 526.7, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), *a* = 34.95(3), *b* = 10.408(7), *c* = 20.75(3) Å, β = 116.95(7)°, *U* = 6 728(6) Å^3, D_c (*Z* = 8) = 1.04 g cm^{-3}, *F*(000) = 2 288, μ_{Mo} = 0.65 cm^{-1}. Specimen: irregular, *ca.* 0.4 mm, *N* = 3 155, N_o 982, *R* = 0.12, *R′* = 0.12.

(**13**). $C_{25}H_{40}LiN_3$, *M* = 389.5, monoclinic, space group $P2_1/n$ (variant of C^5_{2h}, no. 14), *a* = 19.42(1), *b* = 15.272(9), *c* = 8.722(6) Å, β = 92.75(5)°, *U* = 2 584(3) Å^3, D_c (*Z* = 4) = 1.00 g cm^{-3}, *F*(000) 856, μ_{Mo} = 0.62 cm^{-1}. Specimen: cuboid, *ca.* 0.3 mm, *N* = 2 430, N_o = 1 128, *R* = 0.059, *R′* = 0.055.

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

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