DALTON
FULL PAPER

Reactions of silylallyl-lithium or -potassium compounds with Bu^{t}CN; synthesis and structures of $[M\{N(SiMe_2R)C(Bu^t)(CH)_3SiMe_2Bu^t\}]$ [M = Li(tmen), R = Me; or M = K, R = Bu^t], $[Li\{N(SiMe_3)C(Bu^t)\overline{CCHC(SiMe_3)(CH_2)_2C}H_2\}(tmen)]$ and $[\{Li[N{=}C(Bu^t)\overline{CHCHC(SiMe_3)(CH_2)_2C}H_2]\}_4]$ (tmen = $Me_2NCH_2CH_2NMe_2$)

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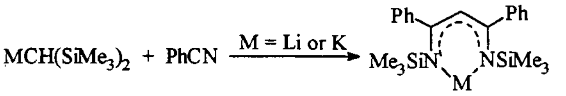
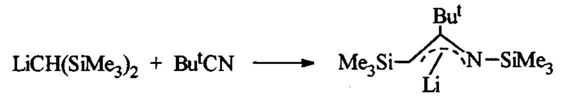
The reactions of a 1,3-bis(silyl)allyl-lithium-tmen or corresponding potassium reagent with Bu^{t}CN yielded the appropriate silyl migration product $[Li\{N(SiMe_2R^1)C(Bu^t)(CH)_3SiMe_2R^2\}(tmen)]$ ($R^1 = R^2 = Bu^t$, $R^1 = Me$, $R^2 = Bu^t$ or $R^1 = R^2 = Me$), $[Li\{N(SiMe_3)C(Bu^t)\overline{CCHC(SiMe_3)(CH_2)_2C}H_2\}(tmen)]$ or $[K\{\eta^4\text{-}N(SiMe_2R^1)C(Bu^t)(CH)_3SiMe_2R^2\}]$ ($R^1 = R^2 = Bu^t$, $R^1 = Bu^t$, $R^2 = Me$ or $R^1 = R^2 = Me$). The 1,5-bis(silyl)-1-azapenta-2,4-dienyllithium tmen-free analogues were obtained by lithiation of the corresponding enamines. The reaction of 2-trimethylsilylcyclohexenyl-lithium with Bu^{t}CN produced the imidolithium complex $[\{Li[N{=}C(Bu^t)\overline{CHCHC(SiMe_3)(CH_2)_2C}H_2]\}_4]$. Single crystal structures of four complexes have been determined.

1,3-Trimethylsilyl migrations from carbon to nitrogen were observed when $MCH(SiMe_3)_2$ (M = Li or K) was treated with PhCN or Bu^{t}CN, yielding a β-diketiminate or 1-azaallyl eqn. (1) or (2), respectively.[1] Recently we briefly described a



(1)



(2)

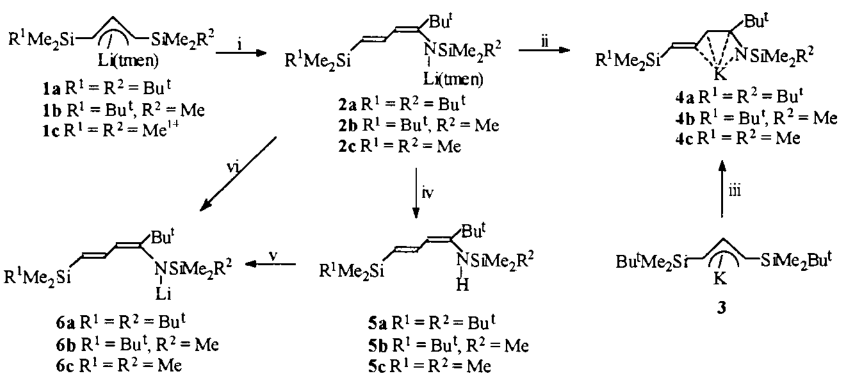
similar 1,3 migration of a trimethylsilyl or *tert*-butyldimethylsilyl group in an allyl rather than an alkyl system;[2] this allowed us to prepare 1,5-bis(silyl)-1-azapenta-2,4-dienylalkali metal complexes, including the X-ray-characterised compound $[\{K[\eta^4\text{-}N(SiMe_2Bu^t)C(Bu^t)(CH)_3SiMe_2Bu^t]\}_\infty]$, potentially useful ligand transfer reagents.

1-Azapentadienyl anions were known as intermediates in organic synthesis[3] or as precursors in metal complexation reactions.[4] Although 1-azapentadienyl-lithium or -potassium had not been isolated prior to our work, their structures in solution had been studied using NMR spectroscopy, or their presence had been inferred by trapping reactions with various electrophiles. It appeared that the 1-azapentadienyl anions were conformationally mobile. In most cases, a zigzag-shaped (W) conformation was favoured.[5] 1,2,4-Triphenyl-1-azapentadienyllithium adopted a horseshoe-like (U) conformation in thf solution, according to its NMR spectrum.[5a]

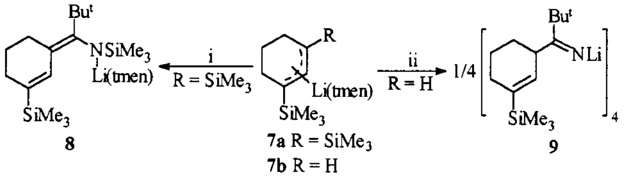
In a previous paper the synthesis and characterisation of the various 1,3-bis(silyl)allyl-lithium and -potassium precursors for the present study were reported.[6] We now present (i) details of the reactions of various 1,3-bis(silyl)allyl-lithium or -potassium complexes with Bu^{t}CN and the structure of crystalline $[\{K[\eta^4\text{-}N(SiMe_2Bu^t)C(Bu^t)(CH)_3SiMe_2Bu^t]\}_\infty]$, (ii) the related reactions of 1-trimethylsilylcyclohexenyl- or 1,3-bis(trimethylsilyl)cyclohexenyl-lithium with Bu^{t}CN, (iii) characterisation of the new 1-azapentadienylmetal compounds and (iv) the structures of crystalline $[Li\{N(SiMe_3)C(Bu^t)(CH)_3SiMe_2Bu^t\}(tmen)]$, $[Li\{N(SiMe_3)C(Bu^t)\overline{CCHC(SiMe_3)(CH_2)C}H_2\}(tmen)]$ and $[\{Li[N{=}C(Bu^t)\overline{CHCHC(SiMe_3)(CH_2)_2C}H_2]\}_4]$.

Results and discussion

The synthesis of the new 1-azapenta-2,4-dienyllithium compounds **2a**–**2c**, **6a**–**6c**, **7a**, **7b**, **8** and **9** and a series of potassium analogues **4a**–**4c** are summarised in Schemes 1 and 2. Thus, treatment of $[Li\{\eta^3\text{-}CH(CHSiMe_2R^1)(CHSiMe_2R^2)\}(tmen)]$ ($R^1 = R^2 = Bu^t$ **1a** or Me **1c**, or $R^1 = Bu^t$ and $R^2 = Me$ **1b**)[6] with Bu^{t}CN yielded (step i in Scheme 1) $[Li\{N(SiMe_2R^2)CBu^t(CH)_3SiMe_2R^1\}(tmen)]$ ($R^1 = R^2 = Bu^t$ **2a** or Me **2c**, or $R^1 = Bu^t$ and $R^2 = Me$ **2b**); for the case of **2a**, heating under reflux in thf was necessary, whereas the less bulky **2b** and **2c** were readily formed in diethyl ether or thf at ambient temperature. The 1-azapenta-2,4-dienylpotassium compounds $[K\{N(SiMe_2R^2)CBu^t(CH)_3SiMe_2R^1\}]$ ($R^1 = R^2 = Bu^t$ **4a** or Me **4c**, or $R^1 = Bu^t$ and $R^2 = Me$ **4b**) were obtained (step ii of Scheme 1) from KOBu^t and the appropriate lithium compound **2a**–**2c**; **4a** was also directly accessible (step iii of Scheme 1) from $[K\{CH(CHSiMe_2Bu^t)_2\}]$ **3**[6] and Bu^{t}CN, but refluxing in thf was required in order that the reaction went to completion and interestingly the isolated crystalline **4a** was thf-free. The tmen-free analogues **6a**–**6c** of **2a**–**2c** were prepared from the latter by successive reactions with water [yielding the thermally stable, distillable 1,5-bis(silyl)-1-azapenta-2,4-dienes **5a**–**5c**] and *n*-butyllithium (steps iv and v of Scheme 1); the transformations **2** ⟶ **6** could



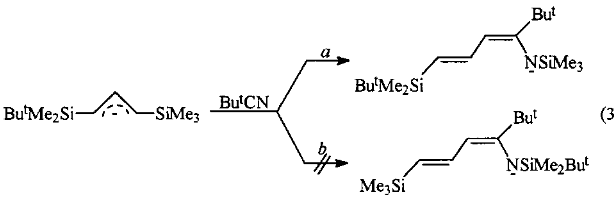
Scheme 1 Synthesis of [M{N(SiMe$_2$R^2)C(Bu^t)(CH)$_3$SiMe$_2$R^1}] [M = Li(tmen) or K] and related compounds. i, Bu^{t}CN, R^2 = Bu^t, thf, reflux, 9 h; R^2 = Me, Et$_2$O or thf, room temperature, 12 h; ii, KOBu^t, hexane, room temperature, 4 h; iii, Bu^{t}CN, thf, 75–80 °C, 6 h; iv, water, thf, room temperature, 30 min; v, LiBu^n, hexane, room temperature, 1 h and reflux 5 h; vi, water, thf, room temperature, 30 min then LiBu^n, hexane, room temperature, 1 h and reflux 5 h.



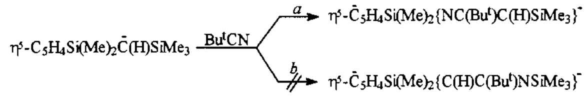
Scheme 2 Reactions of trimethylsilylcyclohexenyllithium complexes **7a** and **7b** with Bu^{t}CN. i, Bu^{t}CN, pentane, room temperature, 4 h; ii, Bu^{t}CN, hexane, room temperature, 4 h.

also be performed in a one-pot manner. The 1,5-bis(silyl)-1-azapenta-2,4-dienyllithium compound $[Li\{N(SiMe_3)C(Bu^t)\overline{C(CH_2)_3C(SiMe_3)C}H\}(tmen)]$ **8** and the lithium imide $[\{Li[NC(Bu^t)\overline{CH(CH_2)_3C(SiMe_3)C}H]\}_4]$ **9** were prepared (steps i and ii of Scheme 2) under mild conditions from the appropriate lithium compound $[Li\{\eta^3\text{-}\overline{C(R)(CH_2)_3C(SiMe_3)C}H\}(tmen)]$ (R = SiMe$_3$ **7a** or H **7b**)[6] and Bu^{t}CN.

Each of the reactions i and ii of Scheme 1 and i of Scheme 2, which resulted in the formation of the 1,5-bis(silyl)-1-azapenta-2,4-dienyllithium (**2a**, **2b**, **2c** and **8**) and potassium (**4a**, **4b** and **4c**) compounds from Bu^{t}CN and the appropriate 1,3-bis(silyl)-allylmetal substrate, clearly involved not only C–C bond formation but also a 1,3-silicotropic shift, as had been the case also for reactions (1) and (2). An interesting additional feature relates to the situation involving the unsymmetrical substrate **2b**; in principle, either or both pathways *a* and *b* of eqn. (3) might have been followed, but in practice the transformation was chemoselective (pathway *a*), involving SiMe$_3$ rather than SiMe$_2$Bu^t migration. This suggests that the allylic anion of **1b** behaves as a CH(SiMe$_3$)-, rather than a CH(SiMe$_2$Bu^t)-, centred nucleophile in attacking the nitrile, presumably for steric reasons. Such effects may also have a role in the lack of reaction of any of the above compounds **2a**–**2c** with Bu^{t}CN, whereas 1-azapenta-2,4-dienyllithium has been reported to be a source of substituted pyridines, upon treatment with RCN (R = Et, Pr^i or Ph).[3d] Likewise, the monosilylallylic compound **7b** is presumed to have functioned as a *C*(H)-, rather than a *C*(SiMe$_3$)-, centred nucleophile in reaction ii of Scheme 2 leading to **9**, obtained as the imido-, rather than the dienylamido- (see below), tautomer. Another case of chemoselectivity, related to that of eqn. (3), has been reported, eqn. (4).[7]

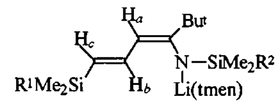


(3)



(4)

The new compounds were characterised by elemental analyses (**2**–**6**), ^{1}H (**2**–**6**, **8** and **9**), ^{13}C-{^{1}H} (**2**–**6** and **8**), ^{7}Li-{^{1}H} (**2** and **6**) and ^{29}Si-{^{1}H} (**2**) NMR, IR (**5**) and GC-MS (**5**) spectra. The ^{1}H NMR spectrum of each of the 1,5-bis(silyl)-1-azapenta-2,4-dienyllithium–tmen adducts **2a**–**2c** showed appropriate silyl group, *tert*-butyl and skeletal CH (for labelling, see **2d**) signals.

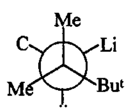


2d

Each of the protons H$_a$ and H$_c$ was coupled to H$_b$ to give doublets, with coupling constants of *ca.* 10 and 18 Hz, respectively; H$_b$ was coupled to both H$_a$ and H$_c$ to give double doublets. The ^{13}C-{^{1}H} NMR spectra of **2a**–**2c** also showed appropriate signals for the skeletal carbon atoms and the *tert*-butyl and silyl groups. The ^{7}Li-{^{1}H} NMR spectra of each of **2a**–**2c** showed a singlet, with very similar chemical shifts.

The ^{1}H and ^{13}C-{^{1}H} NMR spectra of the potassium complexes **4a**–**4c** were recorded in pyridine-d^5 and showed silyl, *tert*-butyl and skeletal CH signals, consistent with the proposed structure of each complex shown in Scheme 1.

The ^{7}Li-{^{1}H} NMR spectral chemical shifts of tmen-free analogues **6a**–**6c** of **2a**–**2c** were in the range δ −0.79 to −0.63, slightly lower in frequency than for **2a**–**2c** (δ −0.42 to −0.07). The ^{1}H and ^{13}C-{^{1}H} NMR spectra showed similar azapentadienyl skeletal signals (both for chemical shifts and coupling constants) to those of **2a**–**2c**, consistent with their having a sickle-like (*S*) skeletal structure, as in crystalline **2b** (see below). It is noteworthy that in the ^{1}H and ^{13}C-{^{1}H} NMR spectra of the 1,5-bis(*tert*-butyldimethylsilyl) complex **6a** the silylmethyls appeared as four signals. By contrast, the spectra of **2a** exhibited only two silylmethyl signals. This may be due to the presence of a non-planar nitrogen atom in complex **6a**, whence the two silylmethyls are in different chemical environments, as illustrated in the Newman projection **6a′**.



6a′

Each of the dienamines **5a**–**5c** gave satisfactory elemental analyses as well as ^{1}H, ^{13}C-{^{1}H} NMR, IR and GC-MS spectra. For example, the ^{1}H NMR spectra of **5a**–**5c** were fully assigned

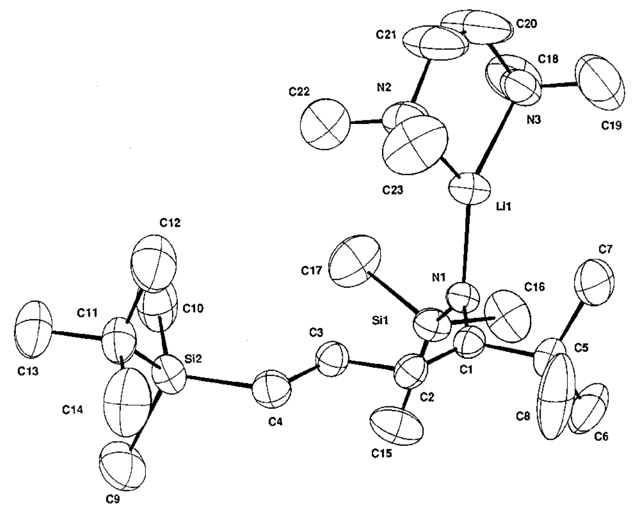


Fig. 1 An ORTEP[10] representation of the molecular structure of crystalline complex **2b**.

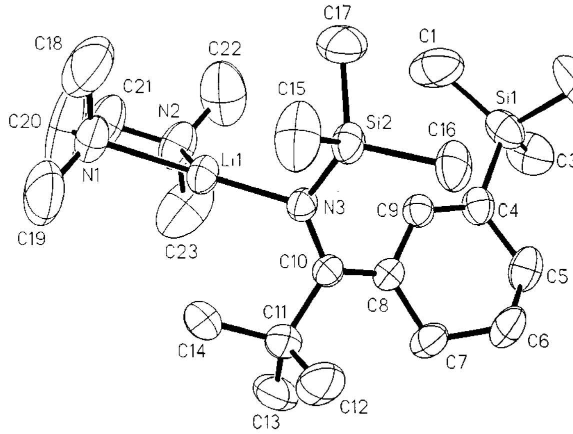


Fig. 2 An ORTEP representation of the molecular structure of crystalline complex **8**.

Table 1 Selected intramolecular distances (Å) and angles (°) for complex **2b**

Li(1)–N(1)	1.910(8)	Li(1)–N(2)	2.058(9)
Li(1)–N(3)	2.079(9)	Li(1)···C(1)	2.750(9)
Si(1)–N(1)	1.673(4)	Si(2)–C(11)	1.877(5)
Si(2)–C(4)	1.842(5)	C(1)–C(2)	1.362(6)
N(1)–C(1)	1.368(5)	C(2)–C(3)	1.424(6)
C(1)–C(5)	1.544(6)	C(3)–C(4)	1.345(6)
N(1)–Li(1)–N(2)	130.0(5)	N(1)–Li(1)–N(3)	142.4(5)
N(2)–Li(1)–N(3)	87.2(3)	N(1)–Si(1)–C(17)	111.7(2)
N(1)–Si(1)–C(15)	113.8(2)	N(1)–Si(1)–Li(1)	33.5(2)
N(1)–Si(1)–C(16)	111.3(2)	C(15)–Si(1)–Li(1)	144.3(2)
C(17)–Si(1)–Li(1)	84.4(3)	C(4)–Si(2)–C(10)	110.8(3)
C(16)–Si(1)–Li(1)	101.7(3)	C(1)–N(1)–Si(1)	127.9(3)
C(4)–Si(2)–C(9)	110.3(3)	Si(1)–N(1)–Li(1)	117.6(3)
C(4)–Si(2)–C(11)	109.5(2)	C(1)–N(1)–Li(1)	113.0(4)
C(23)–N(2)–C(21)	111.5(6)	C(23)–N(2)–Li(1)	109.9(5)
C(21)–N(2)–C(22)	111.9(6)	C(22)–N(2)–Li(1)	111.4(5)
C(21)–N(2)–Li(1)	103.6(4)	C(20)–N(3)–C(18)	110.2(6)
C(20)–N(3)–C(19)	111.4(7)	C(20)–N(3)–Li(1)	102.6(4)
C(19)–N(3)–Li(1)	114.0(5)	C(18)–N(3)–Li(1)	111.4(4)
C(2)–C(1)–N(1)	125.1(4)	C(2)–C(1)–C(5)	118.9(4)
N(1)–C(1)–C(5)	116.0(4)	C(1)–C(2)–C(3)	125.5(4)
C(4)–C(3)–C(2)	127.7(4)	C(3)–C(4)–Si(2)	127.6(4)

Table 2 Selected intramolecular distances (Å) and angles (°) for complex **8**

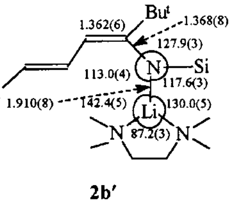
Li(1)–N(1)	2.119(5)	Li(1)–N(2)	2.053(5)
Li(1)–N(3)	1.914(4)	N(3)–Si(2)	1.6828(18)
C(4)–C(9)	1.354(3)	C(4)–C(5)	1.536(4)
C(5)–C(6)	1.500(4)	C(6)–C(7)	1.512(4)
C(7)–C(8)	1.518(3)	C(8)–C(10)	1.382(3)
C(8)–C(9)	1.441(3)	C(10)–N(3)	1.381(3)
C(10)–C(11)	1.555(3)		
N(3)–Li(1)–N(2)	121.5(2)	N(3)–Li(1)–N(1)	150.5(2)
N(2)–Li(1)–N(1)	87.06(17)	N(3)–C(10)–C(11)	115.46(19)
N(3)–C(10)–C(8)	122.85(18)	N(3)–Si(2)–C(16)	116.18(11)
N(3)–Si(2)–C(15)	109.79(13)	N(3)–Si(2)–C(17)	110.75(13)
C(8)–C(10)–C(11)	121.7(2)	C(10)–N(3)–Si(2)	126.84(14)
C(10)–N(3)–Li(1)	120.31(18)	C(21)–N(2)–Li(1)	106.0(2)
C(21)–C(20)–N(1)	127.3(4)	C(10)–C(8)–C(9)	120.1(2)
C(9)–C(4)–C(5)	118.0(2)	Si(2)–N(3)–Li(1)	112.62(15)

(see Experimental section). The IR spectra showed medium intensity NH absorptions in the range 3390–3402 cm^{-1}. A noteworthy feature of compounds **5a**–**5c** is that in the range 25–80 °C (^{1}H NMR spectra) they only existed exclusively in the enamine forms. In general, a secondary enamine is in equilibrium with its imine tautomer, with the latter usually the more stable. This equilibrium is known to be affected by the skeletal substituents and factors such as temperature and solvent.[8] In some cases, the enamine was shown to be preponderant; for example, for $Bu^n_2C{=}CHNHSiEt_3$ the imine was present only to the extent of 4%.[9] In each of the compounds **5a**–**5c** the dominance of the dienamine is probably attributable to its greater conjugative stabilisation and the influence of the *N*-silyl substituents.

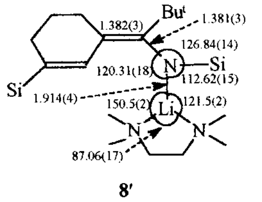
The ^{1}H NMR spectra of complexes **8** and **9** were consistent with the structures shown in Scheme 2.

Crystal structures of complexes 2b and 8

The molecular structures and the atom numbering schemes of crystalline complexes **2b** and **8** are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are presented in Tables 1 and 2, respectively. Both **2b** and **8** are mononuclear buta-1,3-dienylamidolithium compounds, rather than η^5-1-azapentadienyllithium or η^3-1-azaallyllithium isomers. Their 1-azapentadienyl skeletal units adopt a sickle-like (*S*) conformation and have similar bond lengths. The lithium–amido nitrogen distances of 1.910(8) Å for **2b** and 1.914(4) Å for **8** are a little short for a mononuclear four-co-ordinate lithium amide, which generally fall within the range 1.94–2.01 Å.[11] There are some bond angle differences around both the lithium and amido nitrogen between the two complexes. Simplified bonding patterns for **2b** and **8**, shown in **2b′** and **8′**, are shown for comparison. Both the amido nitrogen and the lithium atom are in a trigonal planar environment in each complex, the sum of the angles at the amido nitrogen and Li being 358.5 and 359.6° for **2b** and 359.8 and 359.1° for **8**, respectively.



2b′



8′

Crystal structure of complex 4a

The crystalline potassium complex **4a** is a polymer (Fig. 3, which includes the atom labelling scheme), as already briefly described.[2] Fig. 4 illustrates how the structure propagates. Each anion is related to two K$^+$ cations on crystallographic inversion centres. The potassium ions lie above and below η^4-1-azapentadienyl anions, and with the atoms NC(1)C(2)C(3)C(4) almost coplanar. Selected bond distances and angles are presented in Table 3, which shows that the K–C distances are in the

Table 3 Selected intramolecular distances (Å) and angles (°) for complex **4a**

K(1)–N	2.954(3)	K(1)–C(1)	3.017(4)
K(1)–C(2)	3.183(4)	K(1) · · · C(3)	3.343(4)
K(1) · · · C(8)	3.464(6)	K(1) · · · C(11)	3.532(8)
K(2)–C(1)	2.945(4)	K(2)–N	2.878(3)
K(2)–C(2)	3.248(4)	K(2) · · · C(3)	3.562(4)
K(2) · · · C(6)	3.449(6)	K(2) · · · C(14)	3.418(9)
Si(1)–N	1.655(4)	Si(2)–C(15)	1.886(5)
Si(1)–C(9)	1.893(6)	C(1)–C(2)	1.383(6)
Si(2)–C(4)	1.847(5)	C(2)–C(3)	1.431(6)
N–C(1)	1.341(5)	C(3)–C(4)	1.343(6)
C(1)–C(5)	1.552(6)		
N–Si(1)–C(13)	115.0(3)	N–Si(1)–C(9)	109.9(2)
C(4)–Si(2)–C(19)	110.2(3)	N–Si(1)–C(14)	114.4(3)
C(1)–N–Si(1)	157.6(3)	C(4)–Si(2)–C(20)	108.3(3)
N–C(1)–C(5)	120.2(3)	C(4)–Si(2)–C(15)	110.9(2)
C(1)–C(2)–C(3)	125.1(4)	N–C(1)–C(2)	121.1(4)
C(3)–C(4)–Si(2)	128.9(4)	C(2)–C(1)–C(5)	118.7(4)
C(11)–C(9)–Si(1)	110.3(4)	C(4)–C(3)–C(2)	127.5(4)
C(12)–C(9)–Si(1)	110.8(4)	C(10)–C(9)–Si(1)	111.6(5)
C(18)–C(15)–Si(2)	109.4(4)	C(17)–C(15)–Si(2)	111.5(4)

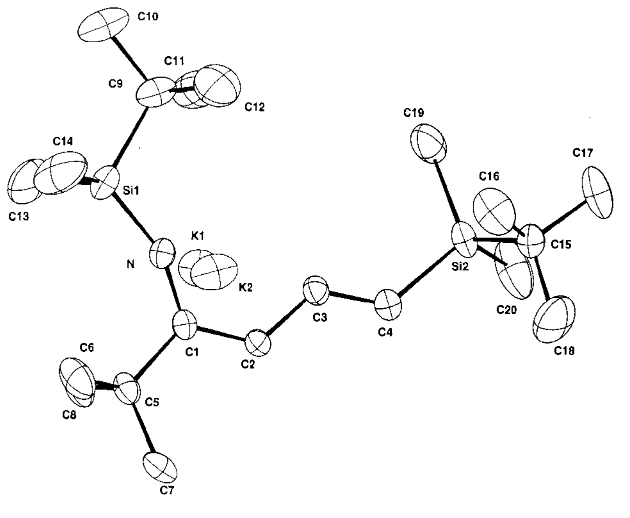


Fig. 3 An ORTEP representation of an azapentadienyl anion in relation to two neighbouring potassium cations in crystalline complex **4a**.

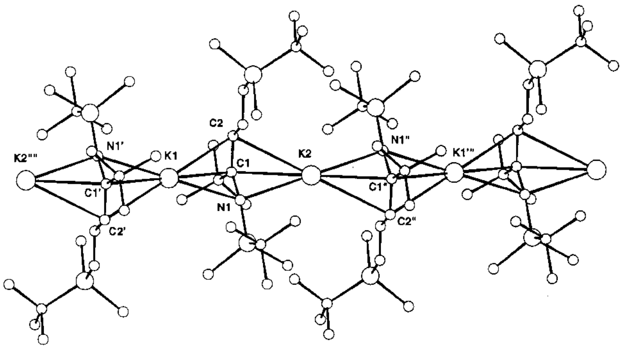


Fig. 4 Representation of crystalline complex **4a**, showing how the structure propagates.

range 2.945(4) to 3.562(4) Å for C(1) to C(3), that to C(1) being the shortest and to C(3) the longest. The potassium atoms also interact with the methyls of the *tert*-butyls on C(1) and Si(1). The K–C distances range from 3.418(9) to 3.532(8) Å. This may be compared with $[\{K[C(SiMe_3)_3]\}_\infty]$, in which each potassium is also in close contact with six methyl groups, ranging from 3.16(2) to 3.31(1) Å.[12] The mean K–N distance of 2.92 Å in **4a** is comparable to the 2.84 Å in $[\{\overline{K[\eta^3\text{-}N(R)C(R')N}C(R')\text{=}CHR](NCR')\}_\infty]$ (R = $SiMe_3$, R′ = $C_6H_3Me_2$-2,5).[13]

Table 4 Selected intramolecular distances (Å) and angles (°) for complex **9**

Li(1)–N(1)	1.986(5)	Li(1)–N(2)	2.013(7)
Li(1)–N(1a)	2.041(5)	Li(1)–Li(1a)	2.519(11)
Li(1)–Li(2a)	2.566(8)	Li(1)–Li(2)	2.573(8)
Li(2)–N(2a)	2.006(6)	Li(2)–N(2)	2.037(6)
Li(2)–N(1)	2.038(6)	Li(2)–Li(2a)	2.508(8)
Li(2)–Li(1a)	2.566(8)	N(1)–C(1)	1.261(3)
C(1)–C(11)	1.542(5)	N(2)–C(15)	1.246(4)
C(1)–C(2)	1.559(3)	C(15)–C(25)	1.526(5)
N(1)–Li(1)–N(2)	100.5(2)	N(1)–Li(1)–N(1a)	101.9(3)
N(2)–Li(1)–N(1a)	99.9(2)	N(1)–Li(1)–Li(1a)	52.26(18)
N(2)–Li(1)–Li(1a)	99.17(18)	N(1a)–Li(1)–Li(1a)	50.33(18)
N(1)–Li(1)–Li(2a)	98.2(3)	N(2)–Li(1)–Li(2a)	50.20(19)
N(1a)–Li(1)–Li(2a)	50.96(19)	Li(1a)–Li(1)–Li(2a)	60.8(2)
N(1)–Li(1)–Li(2)	51.14(18)	N(2)–Li(1)–Li(2)	50.99(19)
N(1a)–Li(1)–Li(2)	96.6(3)	Li(1a)–Li(1)–Li(2)	60.52(19)
Li(2a)–Li(1)–Li(2)	58.4(2)	N(2a)–Li(2)–N(2)	102.8(2)
N(2a)–Li(2)–N(1)	100.2(3)	N(2)–Li(2)–N(1)	98.0(3)
N(2a)–Li(2)–Li(2a)	52.2(2)	N(2)–Li(2)–Li(2a)	51.10(19)
N(1)–Li(2)–Li(2a)	98.70(12)	N(2a)–Li(2)–Li(1a)	50.4(2)
N(2)–Li(2)–Li(1a)	97.0(2)	N(1)–Li(2)–Li(1a)	51.06(19)
Li(2a)–Li(2)–Li(1a)	60.92(18)	N(2a)–Li(2)–Li(1)	97.6(2)
N(2)–Li(2)–Li(1)	50.15(18)	N(1)–Li(2)–Li(1)	49.38(18)
Li(2a)–Li(2)–Li(1)	60.66(18)	Li(1a)–Li(2)–Li(1)	58.7(3)
C(1)–N(1)–Li(1)	137.5(3)	C(1)–N(1)–Li(2)	132.1(2)
Li(1)–N(1)–Li(2)	79.5(2)	C(1)–N(1)–Li(1a)	129.6(3)
Li(1)–N(1)–Li(1a)	77.4(3)	Li(2)–N(1)–Li(1a)	78.0(2)
N(1)–C(1)–C(11)	123.2(2)	N(1)–C(1)–C(2)	121.3(3)
C(15)–N(2)–Li(2a)	138.8(2)	C(15)–N(2)–Li(1)	129.9(3)
Li(2a)–N(2)–Li(1)	79.4(2)	C(15)–N(2)–Li(2)	130.6(2)
Li(2a)–N(2)–Li(2)	76.7(2)	Li(1)–N(2)–Li(2)	78.9(2)
N(2)–C(15)–C(25)	124.3(3)	N(2)–C(15)–C(16)	121.4(3)

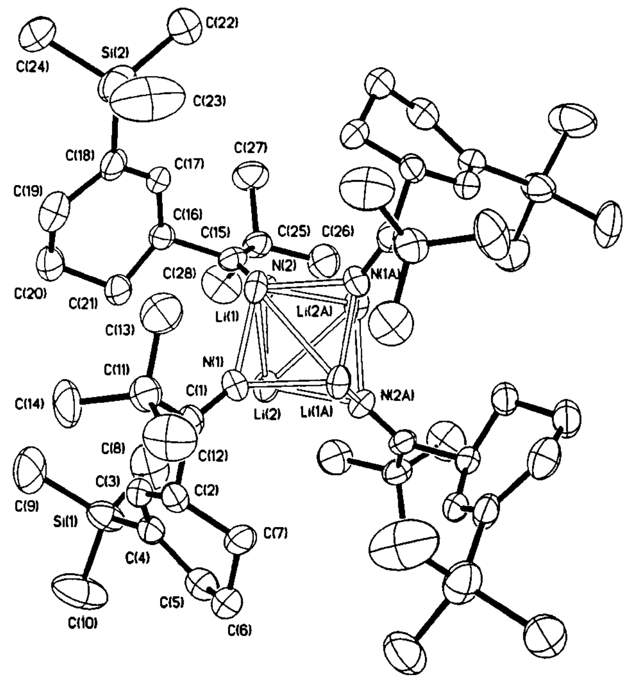


Fig. 5 An ORTEP representation of the molecular structure of crystalline complex **9**.

Crystal structure of complex 9

The molecular structure and the atom numbering scheme of the crystalline complex **9** is shown in Fig. 5. Selected bond distances and angles are presented in Table 4. Crystalline complex **9** is a tetramer. The alternating lithium and nitrogen atoms are arranged in a distorted cube, the Li–Li contacts ranging from 2.508(8) to 2.573(8) Å (but this has no bonding implications). The Li–N distances range from 1.986(5) to 2.041(5) Å, which is appropriate for amidolithium complexes. The average C–N distance, 1.295 Å, implies double bond character. The structure of **9** may be compared with those of some crystalline α-aminolithium imides, which in general are hexamers, as in $[\{Li[\mu\text{-}N{=}C(NMe_2)Ph]\}_6]$,[15] but a tetramer $[\{Li[\mu\text{-}N{=}C(Ph)N(Me)(CH_2)_2NMe_2]\}_4]$ has recently been reported.[16] The conversion **7b** $\longrightarrow$ **9** is unusual in that a $SiMe_3$ shift did not occur.

Experimental

All reactions were performed under argon using standard Schlenk techniques. The thf and diethyl ether were dried using sodium–benzophenone, hexane and pentane by sodium–potassium alloy. The silylallyl-lithium or -potassium complexes **1a**–**1c**, **3** and **7a**, **7b** were prepared as described in a previous paper.[6] The NMR spectra were recorded on AC-P250, WM-360 or AMX-500 instruments, and the solvent resonances were used as the internal references for ^{1}H and ^{13}C spectra; LiCl (1 mol dm^{-3} aqueous solution) was the external reference for ^{7}Li NMR spectra. The IR spectra were recorded on a Perkin-Elmer 1720 FT spectrometer as liquid films using KBr windows. The GC-MS data were recorded on a MD800 apparatus: EI, 70 eV. Elemental analyses were carried out by Medac Ltd., Brunel University. Melting points were determined under argon in sealed capillaries on an electrothermal apparatus and were uncorrected.

Preparations

$[Li\{N(SiMe_2Bu^t)C(Bu^t)(CH)_3SiMe_2Bu^t\}(tmen)]$ 2a. A mixture of $[Li\{\eta^3\text{-}CH(CHSiMe_2Bu^t)_2\}(tmen)]$ **1a**[6] (1.14 g, 2.91 mmol) and Bu^{t}CN (0.35 cm^3, 3.1 mmol) in thf (20 cm^3) was refluxed for 9 h with stirring. The solvent was removed *in vacuo*. The residue was redissolved in hexane and filtered. The filtrate was concentrated *in vacuo* to *ca.* 3 cm^3 to obtain the colourless crystalline complex **2a** (0.64 g, 46%) (Found: C, 65.3; H, 12.2; N, 8.91. $C_{26}H_{58}LiN_3Si_2$ requires C, 65.6; H, 12.3; H, 8.83%), mp 90–92 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.27 (s, 6 H, SiMe$_2$), 0.34 (s, 6 H, SiMe$_2$), 1.10 (s, 9H, Bu^t), 1.22 (s, 9 H, Bu^t), 1.27 (s, 9 H, Bu^t), 1.35 (s, 4 H, tmen), 1.80 (s, 12 H, tmen), 5.46 (d, 1 H, $J = 18.2$), 5.90 (d, 1 H, $J = 10.3$) and 7.35 (dd, 1 H, $J = 10.3$, 18.3 Hz); ^{13}C-{^{1}H}, δ −4.49, −0.72 (SiMe$_2$), 17.41, 21.11, 27.21, 28.75, 30.96, 39.48 (Bu^t), 45.58, 56.37 (tmen), 107.15, 108.82, 149.44 (CH) and 171.56 (*C*Bu^t); ^{7}Li-{^{1}H}, δ −0.42; ^{29}Si-{^{1}H}, δ 1.86, 11.37.

$[Li\{N(SiMe_3)C(Bu^t)(CH)_3SiMe_2R\}(tmen)]$ (R = Bu^t 2b or Me 2c). *tert*-Butyl cyanide (0.75 cm^3, 6.8 mmol) was added dropwise to a solution of $[Li\{\eta^3\text{-}CH(CHSiMe_3)(CHSiMe_2Bu^t)\}(tmen)]$ **1b**[6] (1.57 g, 4.5 mmol) in diethyl ether (20 cm^3) at room temperature with stirring. The solution was stirred overnight. Volatiles were removed *in vacuo* and the residue extracted with hexane. The extract was filtered and the filtrate concentrated *in vacuo* to afford colourless crystals of complex **2b** (1.69 g, 87%) (Found: C, 62.0; H, 11.9; N, 9.13. $C_{23}H_{52}LiN_3Si_2$ requires C, 63.7; H, 12.1; N, 9.69%), mp 86–90 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.30 (s, 6 H, SiMe$_2$), 0.39 (s, 9 H, SiMe$_3$), 1.11 (s, 9 H, Bu^t), 1.27 (s, 9 H, Bu^t), 1.53 (s, 4 H, tmen), 1.80 (s, 12 H, tmen), 5.52 (d, 1 H, $J = 18.3$), 5.93 (d, 1 H, $J = 10.1$) and 7.40 (dd, 1 H, $J = 10.1$, 18.4 Hz); ^{13}C-{^{1}H}, δ −4.56, 4.71 (SiMe), 17.37, 27.20, 30.31, 39.07 (Bu^t), 45.17, 56.04 (tmen), 107.21, 109.68, 149.65 (CH) and 171.80 (*C*Bu^t); ^{7}Li-{^{1}H}, δ −0.07; ^{29}Si-{^{1}H}, δ −19.32, −0.09.

Complex **2c** was obtained using a similar method as that for **2b**. Thus, $[Li\{\eta^3\text{-}CH(CHSiMe_3)_2\}(tmen)]$ **1c**[14] (1.88 g, 6.1 mmol) was treated with Bu^{t}CN (0.7 cm^3, 6.34 mmol) in diethyl ether (30 cm^3) to afford, after work-up, colourless crystals of complex **2c** (1.67 g, 70%) (Found: C, 60.0; H, 11.7; N, 9.70. $C_{20}H_{46}LiN_3Si_2$ requires C, 61.3; H, 11.8; N, 10.7%), mp 59–63 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.33 (s, 9 H, SiMe$_3$), 0.39 (s, 9 H, SiMe$_3$), 1.30 (s, 9 H, Bu^t), 1.49 (s, 4 H, tmen), 1.79 (s, 12 H, tmen), 5.56 (d, 1 H, $J = 18.4$), 5.93 (d, 1 H, $J = 10.2$) and 7.42 (dd, 1 H, $J = 10.2$, 18.4 Hz); ^{13}C-{^{1}H}, δ 0.35, 4.49 (SiMe$_3$), 30.37, 39.09 (Bu^t), 45.19, 56.07 (tmen), 106.51, 112.87, 148.24 (CH) and 172.15 (*C*Bu^t); ^{7}Li-{^{1}H}, δ −0.16; ^{29}Si-{^{1}H}, δ −10.82 and −8.52.

$[K\{\eta^4\text{-}N(SiMe_2Bu^t)C(Bu^t)(CH)_3SiMe_2Bu^t\}]$ 4a. *Method A.* Solid KOBu^t (0.12 g, 1.07 mmol) was added at room temperature to a stirred solution of complex **2a** (0.5 g, 1.05 mmol) in hexane (15 cm^3). A white precipitate appeared after about 30 min. Stirring was continued overnight. The mixture was filtered and the precipitate washed with hexane (2 × 15 cm^3) and dried *in vacuo* to obtain the white solid **4a** (0.20 g, 48%). It was recrystallised from hexane and a trace of pyridine to yield colourless crystalline **4a** (0.07 g).

Method B. tert-Butyl cyanide (0.16 cm^3, 1.46 mmol) was added to a solution of $[K\{CH(CHSiMe_2Bu^t)_2\}]$ **3**[6] (0.45 g, 1.46 mmol) in thf (20 cm^3) at room temperature. The mixture was heated at 75–80 °C (oil-bath temperature) for 6 h with stirring. Volatiles were removed *in vacuo* and the residue was extracted with hot toluene. The extract was filtered and crystallisation of the extract yielded pale yellow crystals of complex **4a** (0.11 g, 19%) (Found: C, 60.9; H, 10.9; N, 3.55. $C_{20}H_{42}KNSi_2$ requires C, 61.3; H, 10.8; N, 3.57%), mp 179–183 °C. NMR (298 K, C_5D_5N): ^{1}H, δ 0.23 (s, 6 H, SiMe$_2$), 0.51 (s, 6 H, SiMe$_2$), 1.00 (s, 9 H, Bu^t), 1.31 (s, 9 H, Bu^t), 1.44 (s, 9 H, Bu^t), 5.07 (d, 1 H, $J = 17.7$), 5.80 (d, 1 H, $J = 10.4$) and 7.77 (dd, 1 H, $J = 10.4$, 17.7 Hz); ^{13}C-{^{1}H}, δ −4.12, −0.23 (SiMe$_2$), 17.47, 23.07, 27.26, 28.29, 31.13, 40.36 (Bu^t), 113.19, 115.68, 160.47 (CH) and 172.55 (*C*Bu^t).

$[K\{N(SiMe_3)C(Bu^t)(CH)_3SiMe_2R\}]$ (R = Bu^t 4b or Me 4c). The procedure was similar to that of *Method A*, see above. Complex **2b** (4.55 g, 10.5 mmol) was treated with KOBu^t (1.2 g, 10.7 mmol) to afford the white solid complex **4b** (2.26 g, 62%) (Found: C, 58.1; H, 10.3; N, 3.91. $C_{17}H_{36}KNSi_2$ requires C, 58.4; H, 10.4; N, 4.00%), mp 240–244 °C. NMR (298 K, C_5D_5N): ^{1}H, δ 0.20 (s, 6 H, SiMe$_2$), 0.53 (s, 9 H, SiMe$_3$), 0.98 (s, 9 H, Bu^t), 1.41 (s, 9 H, Bu^t), 5.23 (d, 1 H, $J = 17.7$), 5.84 (d, 1 H, $J = 10.5$) and 7.66 (dd, 1 H, $J = 10.5$, 17.7 Hz); ^{13}C-{^{1}H}, δ −4.12, 5.44 (SiMe), 17.40, 27.25, 31.01, 39.88 (Bu^t), 98.83, 123.78, 150.06 (CH) and 173.65 (*C*Bu^t). Similarly, complex **2c** (3.7 g, 9.46 mmol) with KOBu^t (1.1 g, 9.82 mmol) yielded the white solid complex **4c** (1.74 g, 60%) (Found: C, 52.5; H, 9.17; N, 4.79. $C_{14}H_{30}KNSi_2$ requires C, 54.6; H, 9.83; N, 4.55%), mp 237–242 °C. NMR (298 K, C_5D_5N): ^{1}H, δ 0.22 (s, 9 H, SiMe$_3$), 0.51 (s, 9 H, SiMe$_3$), 1.41 (s, 9 H, Bu^t), 5.28 (d, 1 H, $J = 18.0$), 5.79 (d, 1 H, $J = 10.5$) and 7.66 (dd, 1 H, $J = 10.5$, 18.0 Hz); ^{13}C-{^{1}H}, δ 0.97, 5.51 (SiMe$_3$), 30.99, 39.90 (Bu^t), 94.42, 103.61, 148.73 (CH) and 173.88 (*C*Bu^t).

$NH(SiMe_2R^2)C(Bu^t)(CH)_3SiMe_2R^1$ (R^1 = R^2 = Bu^t 5a or Me 5c, or R^1 = Bu^t and R^2 = Me 5b). Water (0.15 g, 8.33 mmol) was added with stirring to a solution of complex **2a** (3.39 g, 7.14 mmol) in thf (25 cm^3) at room temperature. After further stirring for 30 min volatiles were removed *in vacuo*. The residue was purified by Al_2O_3 column chromatography to afford the pale yellow oil **5a** (1.7 g, 75%) (Found: C, 67.8; H, 12.1; N, 3.97. $C_{20}H_{43}NSi_2$ requires C, 67.9; H, 12.3; N, 3.96%), bp 103–106 °C (0.03 Torr). NMR (298 K, C_6D_6): ^{1}H, δ 0.18 (s, 6 H, SiMe$_2$), 0.26 (s, 6 H, SiMe$_2$), 0.91 (s, 9 H, Bu^t), 1.00 (s, 9 H, Bu^t), 1.03 (s, 9 H, Bu^t), 2.64 (s, 1 H, NH), 5.61 (d, 1 H, $J = 10.2$), 5.72 (d, 1 H, $J = 18.3$) and 7.14 (dd, 1 H, $J = 10.2$, 18.3 Hz); ^{13}C-{^{1}H}, δ −5.09, −2.76 (SiMe$_2$), 17.06, 18.48, 26.86, 26.89, 29.40, 37.37 (Bu^t), 110.15, 122.06, 144.73 (CH) and 152.31 (*C*Bu^t). IR (liquid film): $\tilde{\nu}_{max}$/cm^{-1} 3402m, 3061w, 2954vs, 2927vs, 2883s, 2856vs, 1622vs, 1568m, 1471s, 1388s, 1361s, 1338m, 1254s, 1218m, 1062m, 1007m, 992m, 923m, 844vs and 825vs. GC-MS: $m/z = 353$ (M^+).

Compound **5b** was obtained similarly. Thus, **2b** (1.55 g, 3.58 mmol) was treated with water (0.1 cm^3, 5.55 mmol) to afford the

Table 5 Crystallographic data for complexes **2b**, **8**, **4a** and **9**

	2b	**8**	**4a**	**9**
Empirical formula	$C_{23}H_{52}LiN_3Si_2$	$C_{23}H_{50}LiN_3Si_2$	$C_{20}H_{42}KNSi_2$	$C_{56}H_{104}Li_4N_4Si_4$
Formula weight	433.8	431.8	391.8	973.6
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
T/K	293	293	298	294
a/Å	10.222(4)	10.365(1)	11.142(2)	29.080(1)
b/Å	12.261(3)	16.901(1)	11.189(2)	11.314(1)
c/Å	14.193(3)	17.684(1)	12.208(2)	24.570(1)
α/°	64.44(2)		73.73(1)	
β/°	75.80(3)	104.03(1)	63.70(1)	122.56(1)
γ/°	89.79(3)		69.44(1)	
V/Å^3	1555.7(8)	3005.4(4)	1263.4(4)	6813.3(5)
Z	2	4	2	4
D/g cm^{-3}	0.926	0.954	1.03	0.949
μ/mm^{-1}	0.126	0.130	0.31	0.120
Reflections collected	7490	8887	4440	11840
Independent, n (R_{int})	7490	4811 (0.0481)	4440	5972 (0.3494)
Observed, n [$I > 2\sigma(I)$]	2647	4441	2615	1278
No. parameters, p	262	263	220	308
$R1$ [$I > 2\sigma(I)$]	0.087	0.080	0.063	0.078
$wR2$ [$I > 2\sigma(I)$]	0.235	0.202	0.119	0.179

pale yellow oil **5b** (0.86 g, 77%) (Found: C, 65.6; H, 12.0; N, 4.54. $C_{17}H_{37}NSi_2$ requires C, 65.6; H, 12.0; N, 4.49%), bp 87–89 °C (0.01 Torr). NMR (298 K, C_6D_6): ^{1}H, δ 0.17 (s, 6 H, $SiMe_2$), 0.19 (s, 9 H, $SiMe_3$), 0.96 (s, 9 H, Bu^t), 0.99 (s, 9 H, Bu^t), 2.31 (s, 1 H, NH), 5.58 (d, 1 H, J = 10.2), 5.72 (d, 1 H, J = 18.3) and 7.11 (dd, 1 H, J = 10.2, 18.3 Hz); ^{13}C-{^{1}H}, δ −5.20, 1.39 (SiMe), 17.04, 26.86, 28.91, 36.80 (Bu^t), 110.35, 122.32, 144.75 (CH) and 152.73 (*C*Bu^t). IR (liquid film): $\tilde{\nu}_{max}$/cm^{-1} 3390m, 3061w, 2954vs, 2928vs, 2900s, 2856s, 1623vs, 1570m, 1470m, 1377s, 1360s, 1334m, 1253s, 1217m, 1155m, 1065m, 996m, 924m, 867vs, 844vs, 779s, 753m, 710w, 685w, 667m and 654m. GC-MS: m/z = 311 (M^+).

Likewise, complex **2c** (8.92 g, 22.8 mmol) was treated with water (0.5 cm^3, 27.8 mmol). The resultant mixture was distilled to yield the pale yellow oil **5c** (4.0 g, 66%) (Found: C, 62.8; H, 11.4; N, 5.22. $C_{14}H_{31}NSi_2$ requires C, 62.4; H, 11.6; N, 5.20%), bp 70–72 °C (0.3 Torr). NMR (298 K, C_6D_6): ^{1}H, δ 0.17 (s, 18 H, $SiMe_3$), 0.98 (s, 9 H, Bu^t), 2.30 (s, 1 H, NH), 5.51 (d, 1 H, J = 10.1), 5.65 (d, 1 H, J = 18.3) and 7.04 (dd, 1 H, J = 10.1, 18.3 Hz); ^{13}C-{^{1}H}, δ −0.37, 1.46 ($SiMe_3$), 28.96, 36.78 (Bu^t), 110.11, 125.14, 143.54 (CH) and 152.81 (*C*Bu^t). IR (liquid film): $\tilde{\nu}_{max}$/cm^{-1} 3390m, 3061w, 2955vs, 2905m, 2872m, 1624vs, 1571m, 1479m, 1466m, 1378s, 1359m, 1335m, 1251s, 1217m, 1155m, 1065m, 995m, 923m, 874vs, 839vs, 770w, 708m, 689m and 665m, GC-MS: m/z = 269 (M^+).

[Li{N(SiMe$_2$R^2)C(Bu^t)(CH)$_3$SiMe$_2$R^1}] (R^1 = R^2 = Bu^t 6a or Me 6c, or R^1 = Bu^t and R^2 = Me 6b). *n*-Butyllithium (2.5 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 4 mmol) was added with stirring to a solution of compound **5a** (1.38 g, 3.91 mmol) in hexane (20 cm^3) at room temperature. The mixture was stirred for 1 h at room temperature and then refluxed for 5 h. After filtration the filtrate was concentrated to *ca.* 3 cm^3 to yield the colourless crystalline complex **6a** (0.86 g, 61%) (Found: C, 66.4; H, 11.8; N, 3.83. $C_{20}H_{42}LiNSi_2$ requires C, 66.8; H, 11.8; N, 3.89%), mp 187–191 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.12 (s, 3 H, SiMe), 0.14 (s, 3 H, SiMe), 0.16 (s, 3 H, SiMe), 0.28 (s, 3 H, SiMe), 0.96 (s, 9 H, Bu^t), 1.04 (s, 9 H, Bu^t), 1.27 (s, 9 H, Bu^t), 5.96 (d, 1 H, J = 18.1), 6.05 (d, 1 H, J = 10.4) and 7.01 (dd, 1 H, J = 10.4, 18.1 Hz); ^{13}C-{^{1}H}, δ −5.11, −5.31, −3.99, 3.12 (SiMe), 16.88, 21.16, 26.76, 28.71, 30.08, 39.66 (Bu^t), 111.35, 128.84, 138.56 (CH) and 171.56 (*C*Bu^t); ^{7}Li-{^{1}H}, δ −0.79.

Complex **6b** was synthesized using a similar route. Thus, **5b** (0.66 g, 2.12 mmol) was treated with LiBu^n (1.4 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 2.24 mmol) to produce colourless crystals of complex **6b** (0.45 g, 67%) (Found: C, 63.8; H, 11.4; N, 4.44. $C_{17}H_{36}LiNSi_2$ requires C, 64.3; H, 11.4; N, 4.41%), mp 138–142 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.12 (s, 6 H, $SiMe_2$), 0.25 (s, 9 H, $SiMe_3$), 0.94 (s, 9 H, Bu^t), 1.19 (s, 9 H, Bu^t), 6.03 (d, 1 H, J = 10.3), 6.04 (d, 1 H, J = 18.1) and 6.99 (dd, 1 H, J = 10.3, 18.1 Hz); ^{13}C-{^{1}H}, δ −5.57, 4.40 (SiMe), 16.89, 26.73, 29.93, 39.20 (Bu^t), 108.73, 127.34, 139.11 (CH) and 171.43 (*C*Bu^t); ^{7}Li-{^{1}H}, δ −0.63.

Likewise compound **5c** (1.4 g, 5.2 mmol) with LiBu^n (3.4 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 5.44 mmol) gave the colourless crystalline complex **6c** (0.94 g, 65%) (Found: C, 60.8; H, 10.9; N, 4.93. $C_{14}H_{30}LiNSi_2$ requires C, 61.0; H, 11.0; N, 5.08%), mp 152–154 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.12 (s, 9 H, $SiMe_3$), 0.23 (s, 9 H, $SiMe_3$), 1.17 (s, 9 H, Bu^t), 5.94 (d, 1 H, J = 10.4), 5.98 (d, 1 H, J = 19.8) and 6.94 (dd, 1 H, J = 10.4, 19.8 Hz); ^{13}C-{^{1}H}, δ −0.93, 4.41 ($SiMe_3$), 29.85, 39.24 (Bu^t), 107.90, 130.31, 138.27 (CH) and 171.73 (*C*Bu^t); ^{7}Li-{^{1}H}, δ −0.69.

[Li{N(SiMe$_3$)C(Bu^t)$\overline{\text{CCHC(SiMe}_3\text{)(CH}_2\text{)}_2\text{C}}H_2$}(tmen)] 8. *tert*-Butyl cyanide (0.83 cm^3, 7.45 mmol) was added dropwise to a solution of complex **7a**[6] (2.6 g, 7.45 mmol) in pentane (*ca.* 30 cm^3) at room temperature. The mixture was stirred for 4 h. Concentration of the solution gave white crystals of complex **8** (3.2 g, 99%). NMR (298 K, C_6D_6): ^{1}H, δ 0.30 (s, 9 H, $SiMe_3$), 0.37 (s, 9 H, $SiMe_3$), 1.46 (s, 12 H, tmen), 1.51 (s, 4 H, tmen), 1.78 (s, 9 H, Bu^t), 1.78–1.85 (m, 2 H), 2.36 (m, 2 H), 2.82 (m, 2 H) and 7.13 (s, 1 H); ^{13}C-{^{1}H}, δ −0.80, 4.73, 25.64, 28.31, 30.52, 31.17, 32.82, 38.93, 45.25, 56.13, 112.0, 142.5 and 164.7.

[{Li[N=C(Bu^t)$\overline{\text{CHCHC(SiMe}_3\text{)(CH}_2\text{)}_2\text{C}}H_2$]}$_4$] 9. *tert*-Butyl cyanide (1.0 cm^3, 9.06 mmol) was added dropwise to a solution of complex **7b**[6] (2.8 g, 10.15 mmol) in hexane (*ca.* 20 cm^3) at room temperature. The mixture was stirred for 4 h. The solvent was removed *in vacuo* and the crystalline solid was dried at 90 °C (0.1 Torr) for 0.5 h. Recrystallisation from hexane gave white crystals of **9** (2.0 g, 81%). ^{1}H NMR (C_6D_6): δ 0.12 (s, 9 H, $SiMe_3$), 1.16 (s, 9 H, Bu^t), 1.62–1.81 (m, 4 H), 2.13 (s, br, 2 H), 3.76 (m, 1 H) and 6.01 (s, 1 H).

Crystallography

Details are given in Table 5. Single crystals of complexes **2b**, **4a**, **8** and **9** were mounted in Lindemann capillaries under argon. Data were collected on Enraf-Nonius CAD4 (for **2b** and **4a**), Rigaku Raxis IIc (for **8**) or AFC7R (for **9**) diffractometers in the θ–2θ mode with monochromated Mo–Kα radiation. The structure was solved by direct methods (SHELXS 86[17] or

Siemens SHELXSTL plus) and refined by full-matrix least squares on all F^2 (SHELXL 93[18]). All non-H atoms were anisotropic.

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