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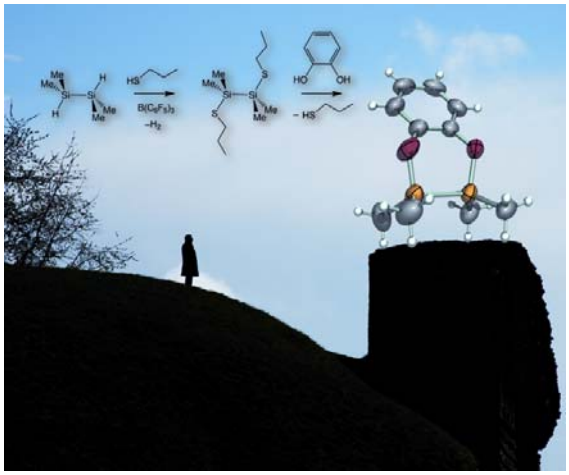

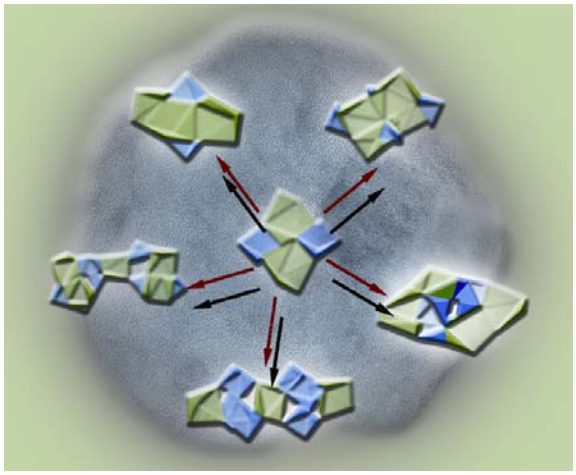

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Synthesis and structures of crystalline Li, Al and Sn(II) 1-azaallyls and β-diketiminates derived from [Li{μ,η³-N(SiMe₃)C(Ad)C(H)SiMe₃}]₂ (Ad = 1-adamantyl)†

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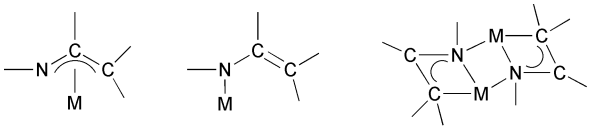
The crystalline dimeric 1-azaallyllithium complex [Li{μ,η³-N(SiMe₃)C(Ad)C(H)SiMe₃}]₂ (**1**) was prepared from equivalent portions of Li[CH(SiMe₃)₂] and 1-cyanoadamantane (AdCN). Complex **1** was used as precursor to each of the crystalline complexes **2–8** which were obtained in good yield. By 1-azaallyl ligand transfer, **1** afforded (i) [Al{η³-N(SiMe₃)C(Ad)C(H)SiMe₃}{κ¹-N(SiMe₃)C(Ad)=C(H)SiMe₃-*E*}Me] (**5**) with [AlCl₂Me]₂, (ii) [Sn{η³-N(SiMe₃)C(Ad)C(H)SiMe₃}₂] (**7**) with Sn[N(SiMe₃)₂]₂, and (iii) [Li(N{C(Ad)=C(H)SiMe₃-*E*}{Si(NN)SiMe₃})(thf)₂] (**8**) with the silylene Si[(NCH₂Bu^t)₂C₆H₄-1,2] [= Si(NN)]. By insertion into the C≡N bond of the appropriate cyanoarene RCN, **1** gave the β-diketiminate [Li{μ-N(SiMe₃)C(Ad)C(H)C(R)NSiMe₃}]₂ [R = Ph (**2**), C₆H₄Me-4 (**3**)], and **5** yielded [Al{κ²-N(SiMe₃)C(Ad)C(H)C(Ph)NSiMe₃}{κ¹-N(SiMe₃)C(Ad)=C(H)SiMe₃-*E*}Me] (**6**). The β-diketiminate [Al{κ²-N(SiMe₃)C(Ad)C(H)C(Ph)NSiMe₃}Me₂] (**4**) was prepared from **2** and [AlClMe₂]₂. The X-ray structures of **1** and **3–8** are presented. Multinuclear NMR spectra in C₆D₆ or C₆D₅CD₃ have been recorded for each of **1–8**; such data on **8** revealed that in solution two minor isomers were also present.

Introduction

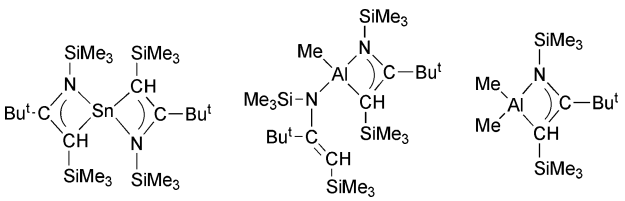
There has been a long-standing interest in lithium 1-azaallyls (prepared *in situ* and generally not structurally characterised) because of their role in organic synthesis,[1] undergoing a number of C–C bond-forming reactions with electrophiles, as in controlled aldol condensation reactions and the regioselective α-functionalisation of ketones.[1] 1-Azaallylic anions have played a major role in heterocyclic chemistry.[2] A direct synthesis of enamines from olefins has recently been reported, as in $Pr^nCH{=}CH_2 + HN(CH_2)_4CH_2 + CO + H_2 \xrightarrow{Cat.} Bu^nCH{=}CHN(CH_2)_4CH_2$.[3]

A 2001 review on 1-azaallylmetal complexes had 144 literature citations.[4] A variety of metal–ligand coordination modes were identified, including the terminal η³- (**I**), terminal κ¹- (enamido) (**II**) and *C*,*N*-chelating-*N*-bridging (**III**).



I II III

Our entry into this field began in 1994, with the disclosure that Li[CH(SiMe₃)₂] with Bu^tCN in Et₂O gave the X-ray-characterised crystalline compound **IV**;[5] related reactions are shown in Scheme 1.[6] Compound **IV** or its Na or K analogue was used as ligand transfer reagent; relevant to the present studies are data on tin(II),[7] and aluminium[8] compounds. The structures of crystalline bis(1-azaallyl)tin(II) complexes are sterically sensitive; *cf.* the X-ray-characterised compounds Sn[η³-N(SiMe₃)C(Bu^t)C(H)SiMe₃]₂ (**V**), Sn[η³-N(SiMe₃)C(Ph)C(SiMe₃)₂][κ¹-N(SiMe₃)C(Ph)=C(SiMe₃)₂] and Sn[κ¹-N(SiMe₃)C(Bu^t)=C(H)C₆H₃Me₂-2,5]₂.[7] The crystalline MeAl complex **VI** in solution underwent rapid 1-azaallyl ligand fluxionality[8b] and, on the basis of multinuclear NMR spectra, the Me₂Al complex **VII** was assigned to have the ligand in the η³-bonding mode **I**.[8b]



V[7] VI[8b] VII[8b]

Results and discussion

The results and discussion is divided into two parts, each based on [Li{μ,η³-N(SiMe₃)C(Ad)C(H)SiMe₃}]₂ (**1**). [Its preparation, from Li[C(H)(SiMe₃)₂][9] and AdCN (Ad = 1-adamantyl), has previously been mentioned in outline[10a] and it has been used as a precursor to P{N(SiMe₃)C(Ad)C(H)SiMe₃}Ph₂.[10b]] The first part deals with the preparation of **1** and its conversion into two lithium β-diketiminates. Succeeding sections are concerned with its role as precursor to (i) three methylaluminium compounds, (ii) a homoleptic tin(II) 1-azaallyl and (iii) a bulky lithium amide derived from the reaction of **1** with the bis(amino)silylene Si[(NCH₂Bu^t)₂C₆H₄-1,2].

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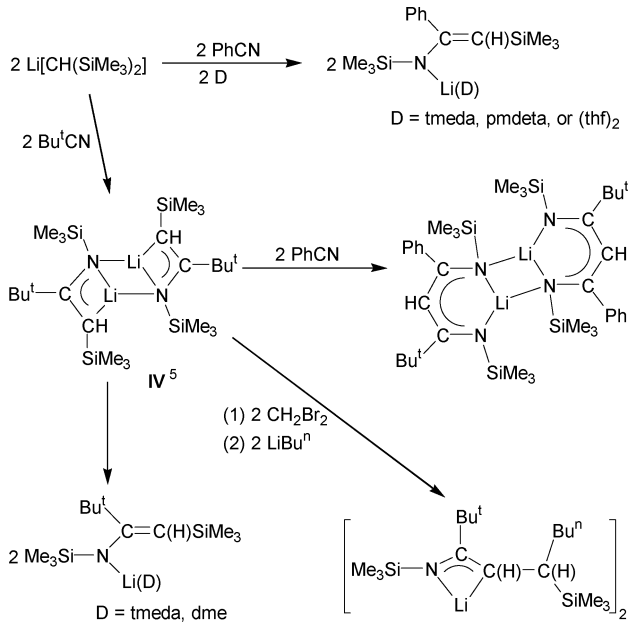
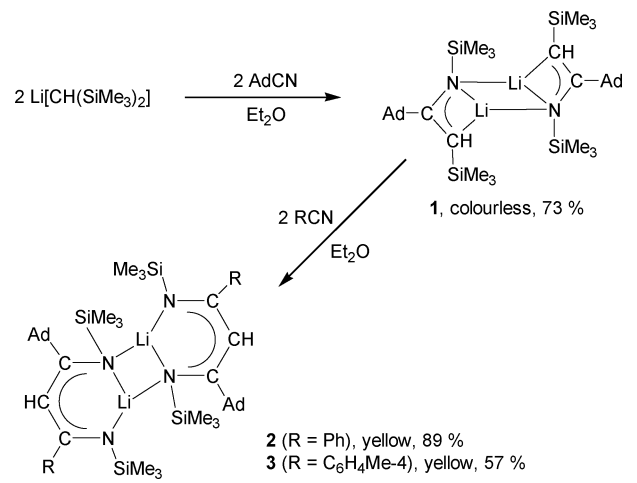
† CCDC reference numbers 668981–668987. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718728a



Scheme 1 Synthesis of 1-azaallyllithium (**IV**)[5] and some of its reactions.[6]

Synthesis and structures of the lithium 1-azaallyl 1 and the β-diketiminates 2 and 3

Their syntheses are shown in Scheme 2; yields (as for **4**–**8**) were not optimised and refer to X-ray-quality crystalline materials. The procedures used are related to those leading to the *tert*-butyl compound **IV** and the β-diketiminate [Li{μ,κ²-{N(SiMe$_3$)C(Ph)CHC(Bu^t)NSiMe$_3$}}]$_2$ rather than [Li{μ,κ²-(N(SiMe$_3$)C(Ph))$_2$C(H)}]$_2$.[6] Each of **1**–**3** was characterised by satisfactory C, H and N analyses, multinuclear NMR solution spectra, mass spectra and for **1** and **3** by single crystal X-ray diffraction studies.



Scheme 2 Synthesis of the crystalline lithium compounds **1**–**3**.

An ORTEP representation of the molecular structure of crystalline **1** is shown in Fig. 1a; its skeletal core, with bond distances, is found in Fig. 1b. From the latter it is evident that each of the ligands is bound to its lithium atom in an η³- rather than the enamido (κ¹)-fashion. The central Li_2N_2 ring is almost planar with the endocyclic angle subtended at each lithium atom (106.4 ± 0.9°) wider that at each nitrogen atom (73.6 ± 0.2 °). The relative disposition of the 1-adamantyl and the adjacent *C*–SiMe$_3$ is *cisoid* (C9 *vs.* Si2) or *transoid* (C27 *vs.* Si4). Some further geometric parameters of **1** are compared with those of **8** in Table 4.

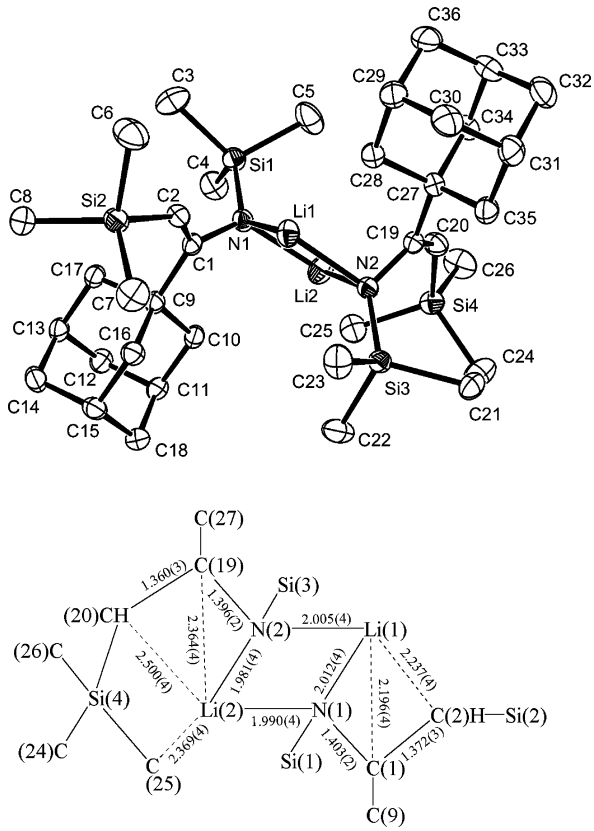


Fig. 1 (a) ORTEP representation of the structure of **1** (50% thermal ellipsoids) (top); (b) bond distances (Å) in the skeletal core of [Li{μ,η³-N(SiMe$_3$)C(Ad)C(H)SiMe$_3$}]$_2$ (**1**) (bottom).

An ORTEP representation of the molecular structure of the centrosymmetric dimeric lithium β-diketiminate **3** is shown in Fig. 2a; its step-like fused tricyclic skeletal core is sketched in 2D in Fig. 2b. Selected geometric parameters for **3** are compared with those of [Li{μ,κ²-(N(SiMe$_3$)C(Ph))$_2$C(H)}]$_2$[6] in Table 1. A less accurate structure of crystalline [Li{μ,κ²-{N(SiMe$_3$)C(Ph)CHC(Bu^t)NSiMe$_3$}}]$_2$ is also available.[6] The central Li_2N_2 ring of **3** is rhomboidal and the adjacent fused six-membered rings are boat-shaped with the Li and C2 atoms 0.83 and 0.11 Å out of the N1N2C1C3 plane respectively. The Li atom

Table 1 Bond distances (Å) and selected angles (°) in the skeletal core of [Li{μ,κ²-N(SiMe$_3$)C(Ad)C(H)C(C$_6$H$_4$Me-4)NSiMe$_3$}]$_2$ (**3**) and [Li{μ,κ²-(N(SiMe$_3$)C(Ph))$_2$C(H)}]$_2$[6]

Compound	**3**	[Li{(N(SiMe$_3$)C(Ph))$_2$C(H)}]$_2$
Li–N1	1.996(2)	1.952(10)
Li–N2	2.015(5)	1.965(9)
N1–C1	1.303(4)	1.299(6)
N2–C3	1.365(3)	1.337(6)
C1–C2	1.448(4)	1.439(6)
C2–C3	1.378(4)	1.394(7)
Li–N2–Li′	78.3(2)	75.0(4)
N2–Li–N2′	101.7(2)	103.0(4)
N1–Li–N2	101.2(2)	105.0(4)

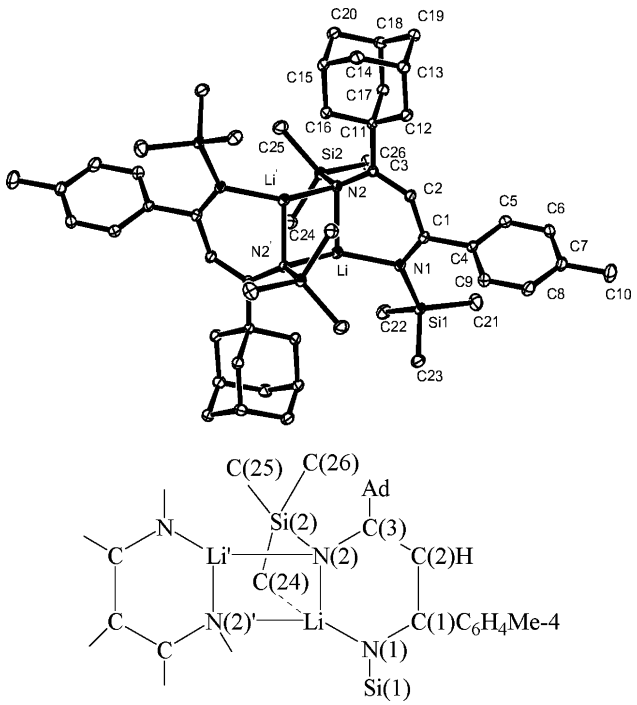


Fig. 2 (a) ORTEP representation of the structure of **3** (50% thermal ellipsoids) (top); (b) the centrosymmetric core of [Li{μ,κ²-N(SiMe$_3$)C(Ad)C(H)C(C$_6$H$_4$Me-4)NSiMe$_3$}]$_2$ (**3**) (bottom).

has relatively close contacts to the C1 [2.702(6) Å], C3 [2.775(6) Å] and C24 [2.861(6) Å] atoms.

Synthesis and structures of the aluminium compounds 4, 5 and 6

The routes to the crystalline methylaluminium compounds **4–6** are illustrated in Scheme 3. Two dimethylaluminium β-diketiminates related to **4** had previously been reported, albeit using a different methodology: [Al{(N(SiMe$_3$)C(Ph))$_2$CH}Me$_2$] (**VIII**) had been obtained by methane elimination from AlMe$_3$ and the appropriate β-diketimine,[11] and CH$_2$[C{C(C$_6$H$_4$Me-4)N(SiMe$_3$)}$_2$AlMe$_2$]$_2$ was similarly prepared from 2AlMe$_3$ and the corresponding CH$_2$-bridged bis(β-diketimine).[12] The synthesis of the methylaluminium bis(1-azaallyl) **5** involved the same strategy (Cl/ligand exchange) as formerly employed for [Al{N(SiMe$_3$)C(Bu^t)C(H)SiMe$_3$}$_2$Me] (**VI**).[8b] The compound **6**, chiral at the Al atom, containing both 1-azaallyl and β-diketiminato ligands is currently without precedent.

Compounds **4–6** were characterised by microanalysis (**5**, **6**), multinuclear (^{1}H, ^{13}C, ^{29}Al and ^{29}Si) NMR spectra in C$_6$D$_6$ at 293 K (**4**, like **VIII**,[11] was fluxional) and mass spectra (**5**, **6**), as well as single crystal X-ray diffraction.

ORTEP representations of the molecular structures of crystalline complexes **4–6** are shown in Fig. 3, 4 and 5, respectively. Selected geometrical data for the AlN1C1C2C3N2 rings of **4**, **VIII**,[11] and **6** are listed in Table 2. The Al atom is 1.0 (**4**), 0.95 (**VIII**) and 1.01 (**6**) Å out of the N1C1C3N2 plane, respectively; for **4** the C2 atom is coplanar with the latter but for the shallow-boat rings of **VIII** and **6**, the C2 atom is 0.12 (**VIII**) or 0.17 (**6**) Å out of the N1C1N2 plane.

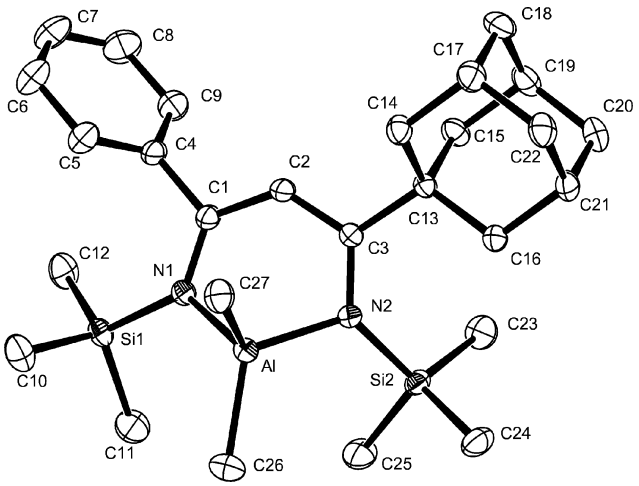
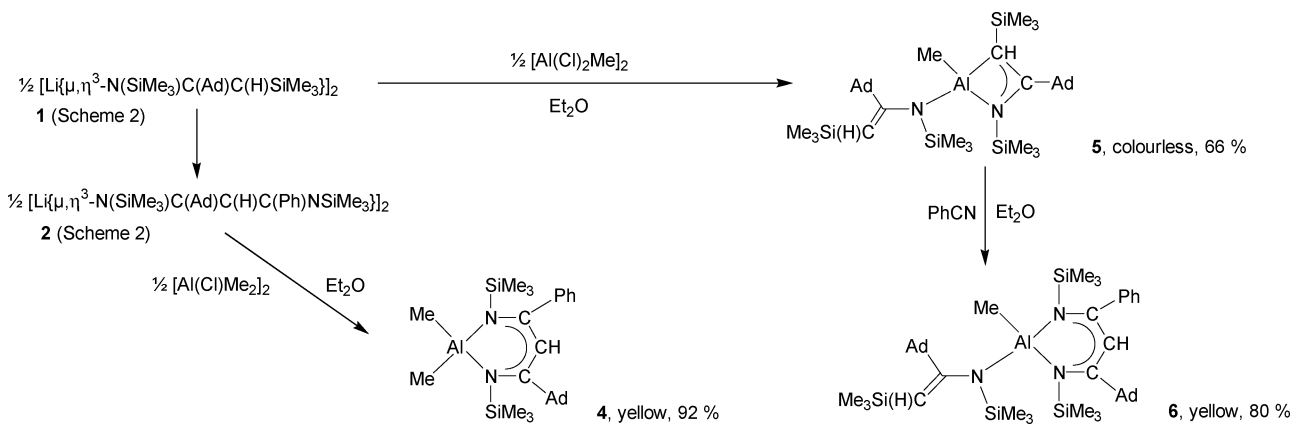


Fig. 3 ORTEP representation of the structure of **4** (50% thermal ellipsoids).

Comparative geometric data for (i) the enamido fragments of [Al{η³-N(SiMe$_3$)C(R)C(H)SiMe$_3$}{κ¹-N(SiMe$_3$)C(R)=C(H)-SiMe$_3$-*E*}Me] [R = Ad (**5**), R = Bu^t (**VI**)[8b]] and [Al{κ²-N(SiMe$_3$)C(Ph)C(H)C(Ad)NSiMe$_3$}{κ¹-N(SiMe$_3$)C(Ad)=C-(H)SiMe$_3$-*E*}Me] (**6**) and (ii) the η³-1-azaallyl fragment of **5** and **VI**[8b] are listed in Table 3. That the two isomeric 1-azaallyl ligands in



Scheme 3 Synthesis of the crystalline aluminium compounds **4–6**.

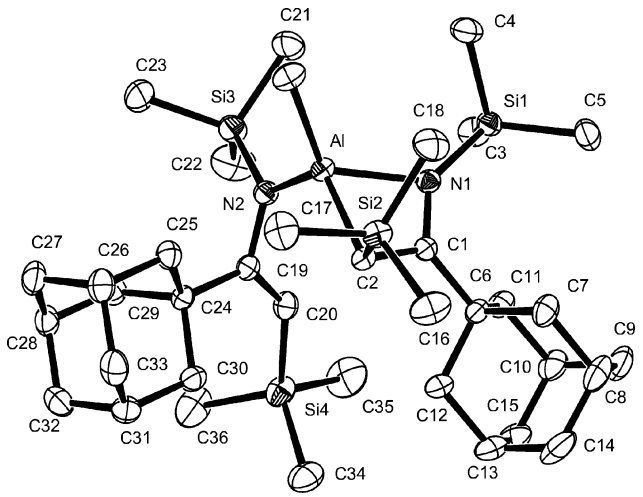


Fig. 4 ORTEP representation of the structure of **5** (50% thermal ellipsoids).

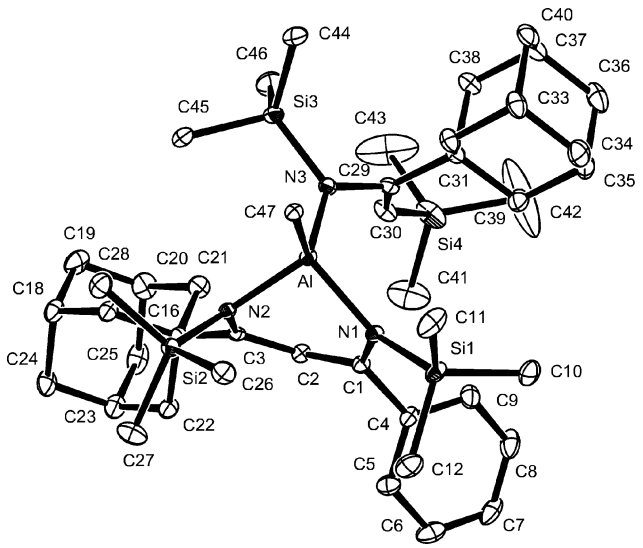


Fig. 5 ORTEP representation of the structure of **6** (50% thermal ellipsoids).

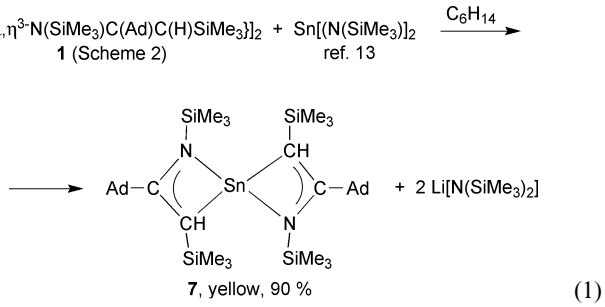
crystalline **5** and **VI** are distinct is attributed to steric factors which make the formation of the isomeric bis(η^3-azaallyl)methylalanes energetically unfavourable for steric reasons. Regarding the η^3-1-azaallylaluminium moiety, the Al atom is 1.55 Å out of the N3C29C30 plane for **6**, 0.76 Å out of the N1C1C2 plane and 1.45 Å out of the N2C19C20 plane for **5**, and 0.66 Å out of the N1C1C2 plane or 1.63 Å out of the N2C13C14 plane for **VI**.[8b] The dihedral angles between the N1C1C2 and the N2C19C20 plane of 80° for **5** is to be compared with the 35° between the N1C1C2 and N2C13C14 planes of **VI**.[8b]

Table 2 Selected bond distances (Å) and angles (°) for the [Al{κ²-N(SiMe$_3$)C(R)C(H)C(Ph)NSiMe$_3$}] fragment of **4**, **6** (R = Ad) and of [Al{κ²-(N(SiMe$_3$)C(Ph))$_2$C(H)}Me$_2$] (**VIII**) (R = Ph)[11]

Compound	**4**	**6**	**VIII**
Al–N1	1.9417(12)	1.959(2)	1.914(4)
Al–N2	1.9235(11)	1.924(2)	1.928(4)
N1–C1	1.3350(16)	1.341(3)	1.331(6)
N2–C3	1.3569(15)	1.359(3)	1.336(6)
C1–C2	1.4124(18)	1.415(3)	1.394(6)
C2–C3	1.4018(4)	1.383(3)	1.406(6)
N1–Al–N2	97.01(5)	95.12(9)	97.1(2)
C1–C2–C3	128.51(12)	126.4(2)	126.8(4)

Synthesis and structure of the bis(η^3-1-azaallyl)tin(II) complex 7

The crystalline homoleptic 1-azaallyltin(II) compound **7** was prepared in high yield as shown in eqn (1). The use of a metal bis(trimethylsilyl)amide in a hydrocarbon solvent as precursor is novel in 1-azaallylmetal chemistry and is likely to have some generality and not only in this area of chemistry; it has the advantage that the co-product Li[N(SiMe$_3$)$_2$] is volatile and hence readily separated *in vacuo*. We have previously used such a strategy for the synthesis of the homoleptic group 14 metal alkyls M[CH(SiMe$_3$)$_2$]$_2$ (M = Ge, Sn); for the germanium alkyl, in particular, it was the method of choice.[13]



(1)

Compound **7** was characterised by microanalysis, EI-mass spectrometry and ^{1}H, ^{13}C, ^{29}Si and ^{119}Sn NMR spectra in deuteriotoluene. The ^{119}Sn chemical shift (δ −377.3 ppm) establishes that in solution both the ligands are bound to the tin atom in the η^3-1-azaallyl mode **I**, as also found in the crystal (Fig. 6). In support, it is noted that similar solutions of Sn[η^3-N(SiMe$_3$)C(Bu^t)C(H)SiMe$_3$]$_2$ (**V**), Sn[κ^1-N(SiMe$_3$)C(Bu^t)=C(H)C$_6$H$_3$Me$_2$-2,5]$_2$, and Sn[η^3-N(SiMe$_3$)C(Ph)C(SiMe$_3$)$_2$][κ^1-N(SiMe$_3$)C(Ph)=C(SiMe$_3$)$_2$] had ^{119}Sn chemical shifts of δ −387.2, 61.5 and −37.3 ppm, respectively.[7]

An ORTEP representation of the molecular structure of crystalline **7** is shown in Fig. 6, together with selected geometric parameters of its core skeletal atoms. The tin atom is 1.39 Å out of both the N1C2C1 and N2C20C19 planes; the dihedral angle between these two planes is 18°. The core structure of **7** is similar to that of **V**[7] or Sn[{N(C$_6$H$_3$Pr$^i_2$-2,6)}$_2$CMe]$_2$ (obtained from Sn[N(SiMe$_3$)$_2$]$_2$ and H[{N(C$_6$H$_3$Pr$^i_2$-2,6)}$_2$CMe]).[14]

Synthesis, reaction pathway and structure of the crystalline lithium silylamide 8

The crystalline lithium compound **8** was obtained in good yield from equivalent portions of the 1-azaallyllithium compound **1** and the thermally stable bis(amino)silylene Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2] (**IX**)[15] [abbreviated as Si(NN)] in thf, eqn (2).

Table 3 Selected bond lengths (Å) and angles (°) for the enamidoAl fragment of **5**, **6** and **VI**[8b] and the 1-azaallylAl fragments of **5** and **VI**[8b]

Compound	**6**	EnamidoAl of **5**	EnamidoAl of **VI**	1-AzaallylAl of **5**	1-AzaallylAl of **VI**
Al–N3	1.856(2)	1.8471(16) [Al–N2]	1.839(2)	1.9945(15) [Al–N1]	1.998(2) [Al–N1]
Al···C29	2.910(2)	2.8314(18) [Al···C19]	2.816(2) [Al···C13]	2.3748(17) [Al–C1]	2.380(2) [Al–C1]
Al···C30	3.736(3)	3.683(2) [Al···C20]	3.564(2) [Al···C14]	2.0399(17) [Al–C2]	2.022(2) [Al–C2]
N3–C29	1.451(3)	1.441(2) [N2–C19]	1.445(3) [N2–C13]	1.326(2) [N1–C2]	1.320(3) [N1–C1]
C29–C30	1.348(4)	1.353(2) [C19–C20]	1.347(3) [C13–C14]	1.467(2) [C1–C2]	1.468(3) [C1–C2]
Al–N3–C29	122.83(17)	118.38(11) [Al–N2–C19]	117.56(14) [Al–N2–C13]	88.96(10) [Al–N1–C1]	89.2(2) [Al–N1–C1]
N3–C29–C30	119.4(2)	119.50(16) [N2–C19–C20]	119.3(2) [N2–C13–C14]	111.71(14) [N1–C1–C2]	111.8(2) [N1–C1–C2]
N3–Al–C30	33.49(8)	34.96(5) [N2–Al–C20]	38.4(1) [N2–Al–C14]	69.95(7) [N1–Al–C2]	70.1(7) [N1–Al–C2]

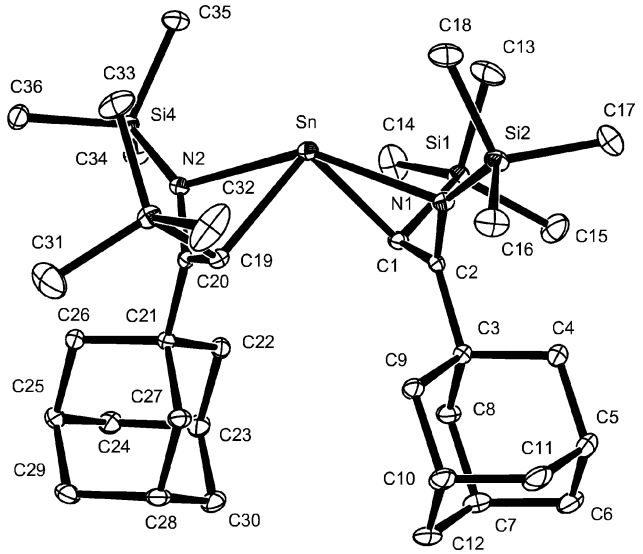
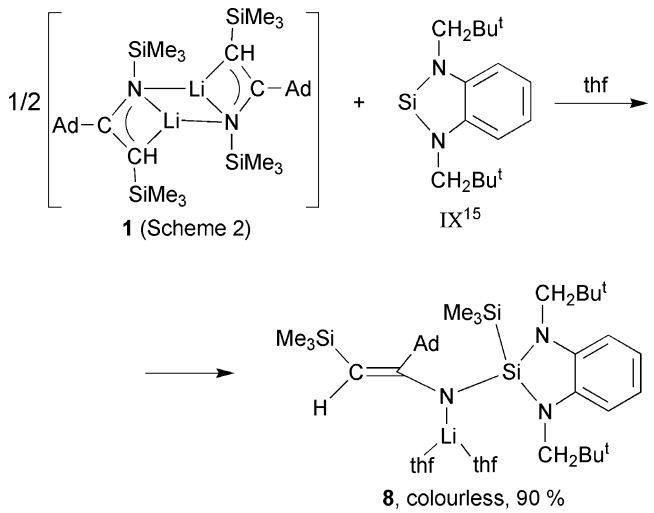
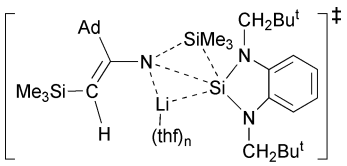


Fig. 6 ORTEP representation of the structure of **7** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (°): Sn–N1 2.5466(16), Sn–N2 2.5156(16), Sn–C1 2.312(2), Sn–C19 2.313(2), Sn–C2 2.741(2), Sn–C20 2.718(2), N1–C2 1.309(2), N2–C20 1.309(2), C1–C2 1.454(3), C19–C20 1.451(3); N1–Sn–C1 57.18(6), N2–Sn–C19 57.63(6), N1–Sn–N2 147.88(5), C1–Sn–C19 92.83(7), C19–Sn–N1 99.99(6), N2–Sn–C1 98.24(6), N1–C2–C1 115.18(17), N2–C20–C19 115.42(17).



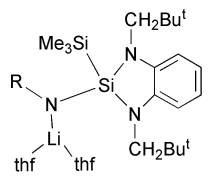
(2)

Plausible routes *a*, *b* and *c* from **1** + **IX** → **8** are shown in Scheme 4. The first step in pathways *a* and *b* is the formation of the donor–acceptor adduct **X**. In *a*, this is succeeded by (i) the electrocyclic 1,3-N–Si(NN) bond-making with N–Li bond breaking yielding the intermediate **XI**, and (ii) a 1,2-$SiMe_3$ shift from **XI** with N–Li bond-making furnishing **8**. In *b*, **X** is converted directly into **8**, the electrocyclic rearrangement involving a 1,3-N → Si $SiMe_3$ shift and Li–Si(NN) bond-breaking. As for route *c*, **1** and **IX** are converted directly into **8**, with **XII** as the transition state. The crucial part of *a* is the intermediate **XI**, which may alternatively be derived directly by a 1,1-addition of the fragments Li and $N(SiMe_3)C(Ad)C(H)SiMe_3$ from **1** to the silylene Si(NN) (**IX**).

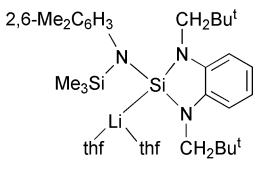


XII

There are precedents for the intermediates related to **X** and **XI**. As for **X**, among numerous examples of Si(NN) (**IX**) behaving as a ligand are the complexes $[Ni\{Si(NN)\}_4]$,[16a] $[CuI(PPh_3)_2\{Si(NN)\}]$,[16a] and $[Ln(\eta^5\text{-}C_5H_5)_3\{Si(NN)\}]$ (Ln = Y, Yb).[16b] Related to **XI** are several compounds obtained from Si(NN) and various salts LiR′ in thf, including $[Li\{Si(NN)R'\}(thf)_n]$ [R′ = Bu^t, n = 3;[17] R′ = $CH(SiMe_3)_2$, n = 2;[17] R′ = $Si(SiMe_3)_3$, n = 2;[17] R′ = NR_2, n = 3 (R = Me, Pr^i)[18]]. In contrast to the formation of such 1,1-adducts of Li-R′ to Si(NN), treatment of Si(NN) with $Li[N(SiMe_3)_2]$ in thf gave **XIIIa**,[19] an analogue of **8**; likewise Si(NN) and $Li[N(Bu^t)SiMe_3]$ gave **XIIIb**.[19] Finally, a crucial experiment was that between Si(NN) and $Li[N(C_6H_3Me_2\text{-}2,6)SiMe_3]$: mixing the reagents below 0 °C gave **XIV** as the major product, but at higher temperatures **XIV** was isomerised yielding **XIIIc**.[18] In the light of the cited earlier data, pathway *a* (or *a*′) is the most appropriate to account for the formation of **8** from **1** + **IX**.

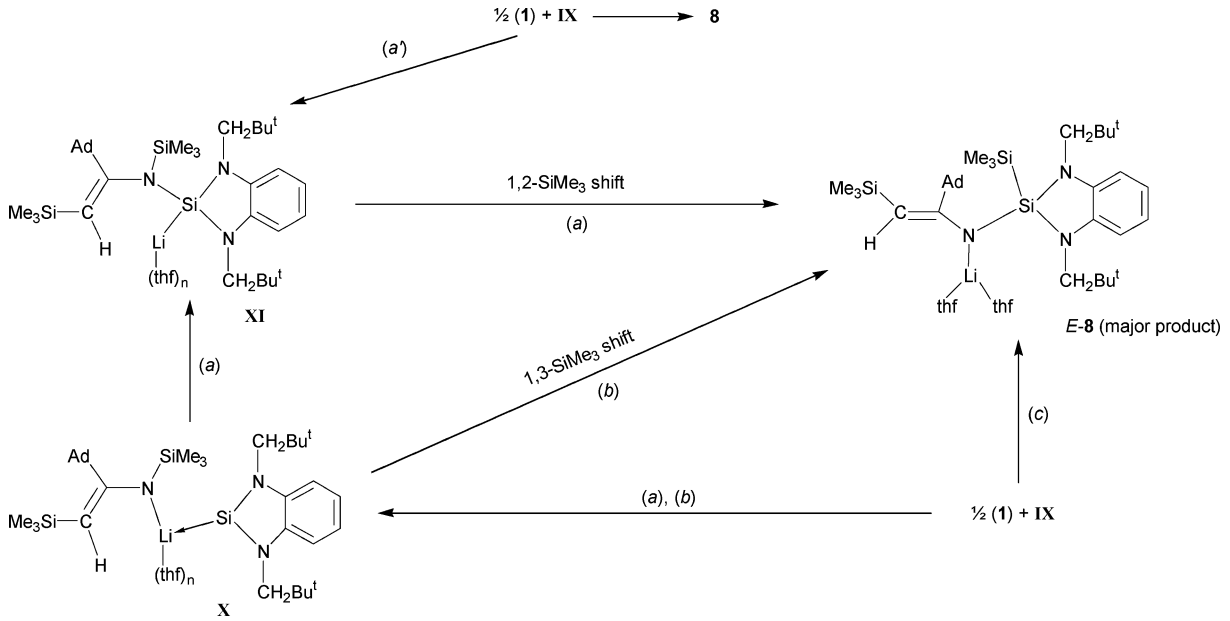


XIIIa R = $SiMe_3$[19]
XIIIb R = Bu^t[19]
XIIIc R = $C_6H_3Me_2$-2,6[18]



XIV[18]

The crystalline lithium amide **8** gave satisfactory microanalytical data (C, H, N). An ORTEP representation of



Scheme 4 Alternative routes [(*a*), (*a*'), (*b*), or (*c*)] from 0.5(**1**) + **IX** → **8**.

its molecular structure is shown in Fig. 7. Skeletal geometrical parameters of the Li[N{Si(NN)SiMe$_3$}] and the [NC(Ad)=C(H)SiMe$_3$-*E*] fragments of **8** are compared with those in [Li(N{Si(NN)SiMe$_3$}SiMe$_3$)(tmeda)] [19] (Table 4a) and [Li{μ,η^3-N(SiMe$_3$)C(Ad)C(H)SiMe$_3$}]$_2$ (**1**) (Table 4b), respectively. The three-coordinate Li and C17(Ad) atoms of **8** are each in a distorted trigonal planar environment, while the N3 atom is 0.16 Å out of the LiC17Si1 plane. The SiMe$_3$ and Ad substituents in **8** are arranged in a *cisoid* manner about the C=C bond. The geometrical parameters of the Li[N{Si(NN)SiMe$_3$}] fragment of **8** are similar to those of [Li(N{Si(NN)SiMe$_3$}SiMe$_3$)(tmeda)].[19]

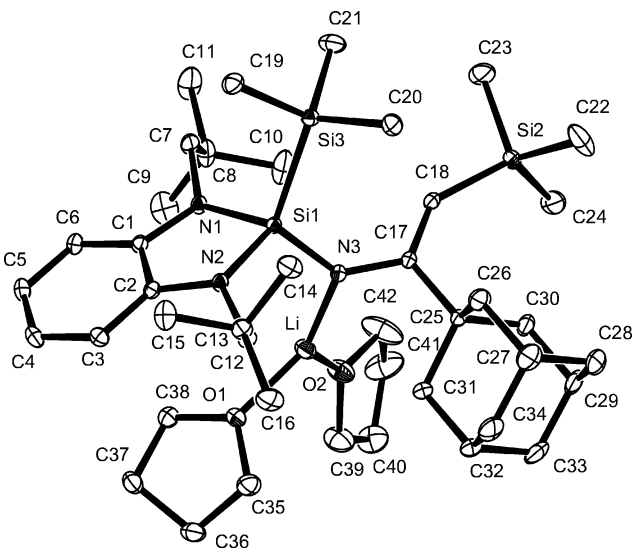


Fig. 7 ORTEP representation of the structure of **7** (50% thermal ellipsoids).

Solutions of **8** in C$_6$D$_6$ were examined by various NMR spectral experiments. At ambient temperature, the ^{1}H NMR spectrum showed three sets of signals, which were assigned to *E*-**8** (major component, *ca.* 55%), *Z*-**8** (*ca.* 19%) and the NH-containing compound (apparently due to adventitious hydrolysis of *E*-**8**); assignments have been made on the basis of NOE experiments. The presence of only two thf signals (α- and β-CH$_2$) suggests that the thf is not strongly bound and undergoes fast exchange even at this temperature. Two ^{7}Li and nine ^{29}Si resonances are consistent with the above assignment. Heating to 90 °C simplified the ^{1}H NMR multiplets in the aromatic and adamantyl proton areas but no coalescence of the signals belonging to different isomers was observed.

In conclusion, the synthesis, structure and a variety of insertion and ligand transfer reactions of the crystalline dimeric μ,η^3-1-azaallyllithium compound **1** are described. These furnished in high yield the new crystalline lithium, aluminium and tin(II) complexes **2–8**, five of which have been X-ray-characterised. The preparation of [Sn{η^3-N(SiMe$_3$)C(Ad)C(H)SiMe$_3$}$_2$] (**7**) by the [N(SiMe$_3$)$_2$]$^-$/[1-azaallyl]$^-$ exchange reaction points to the wider use of metal bis(trimethylsilyl)amides. The reaction between **1** and the silylene Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2] [abbreviated as Si(NN)] in thf gave the crystalline lithium amide [Li(N{C(Ad)=C(H)SiMe$_3$-*E*}{Si(NN)SiMe$_3$})(thf)$_2$] (**8**).

Experimental

General remarks

All manipulations were carried out under argon using standard Schlenk and vacuum line techniques. Pentane and hexane were dried using a sodium–potassium alloy; diethyl ether and thf were dried and distilled from sodium–benzophenone. Solvents were then stored over a sodium mirror under argon. The nitriles and methylaluminium chlorides were commercial samples. The compounds Li[CH(SiMe$_3$)$_2$],[9] Si[(NCH$_2$Bu^t)C$_6$H$_4$-1,2] [15] and Sn[N(SiMe$_3$)$_2$] [13] were prepared by published procedures. Apart from ^{1}H, the NMR spectra were proton-decoupled and were recorded at 293 K in C$_6$D$_6$ unless otherwise stated on a Bruker

Table 4 Selected bond lengths (Å) and angles (°) of (a) the Li[N{Si(NN)SiMe$_3$}] fragment of **8** and of [Li(N(SiMe$_3$){Si(NN)SiMe$_3$})(tmeda)] [19] and (b) the [N–C(Ad)=C(H)SiMe$_3$] fragment of **8** and of **1** [Si(NN) = Si{(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2}]

(a) Compound	**8**		[Li(N(SiMe$_3$){Si(NN)SiMe$_3$})(tmeda)] [19]			
	Li–N3	1.942(4)	Li–N3	1.936(6)		
	Si1–N3	1.6683(17)	Si1–N3	1.656(3)		
	Si1–Si3	2.3791(8)	Si1–Si2	2.3849(11)		
	Li–N3–Si1	113.48(15)	Li–N3–Si1	113.2(2)		
	N3–Si1–Si3	115.09(6)	N3–Si1–Si2	109.76(12)		
(b) Compound	**8**		**1**			
	N3–C17	1.391(3)	N1–C1	1.403(2)	N2–C19	1.396(2)
	C17–C18	1.364(3)	C1–C2	1.372(3)	C19–C20	1.360(3)
	C17–C25	1.548(3)	C1–C9	1.544(3)	C19–C27	1.560(3)
	C18–Si2	1.850(2)	C2–Si2	1.871(2)	C20–Si4	1.855(2)
	N3–C17–C18	123.22(18)	N1–C1–C2	119.29(18)	N2–C19–C20	122.42(18)
	N3–C17–C25	113.52(16)	N1–C1–C9	117.55(16)	N2–C19–C27	116.97(16)
	C17–C18–Si2	141.69(17)	C1–C2–Si2	142.33(16)	C19–C20–Si4	133.34(17)
	C18–C17–C25	123.25(18)	C2–C1–C9	123.13(17)	C20–C19–C27	120.47(17)

DPX 300 (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 116.6 MHz for ^{7}Li) or AMX 500 (131.3 MHz for ^{27}Al, 99.4 MHz for ^{29}Si and 186.5 MHz for ^{119}Sn) instruments and referenced externally (^{7}Li using LiCl, ^{27}Al using AlCl$_3$ with a D$_2$O lock, ^{29}Si using SiMe$_4$, ^{119}Sn using SnMe$_4$) or internally to the residual solvent resonances (^{1}H, ^{13}C). Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were measured in sealed capillaries. Elemental analyses were determined by Medac Ltd, Brunel University, UK.

Preparations

[Li{μ,η^3-N(SiMe$_3$)C(Ad)C(H)SiMe$_3$}]$_2$ (1). A solution of 1-cyanoadamantane (0.78 g, 4.8 mmol) in diethyl ether (*ca.* 8 cm^3) was added to a cooled (−20 °C) solution of bis(trimethylsilyl)methyllithium (0.80 g, 4.8 mmol) in Et$_2$O (15 cm^3). The mixture was stirred at −20 °C for 20 min, then set aside for *ca.* 16 h at 20 °C. Volatiles were removed *in vacuo.* The colourless residue was dissolved in hot hexane (*ca.* 20 cm^3). Cooling at 20 °C afforded colourless crystals of **1** (1.13 g, 73%) (found: C, 65.0; H, 10.69; N, 4.41. C$_{36}$H$_{68}$Li$_2$N$_2$Si$_4$ requires C, 66.0; H, 10.46; N, 4.27%), mp 155–160 °C. ^{1}H-NMR (C$_7$D$_8$): δ 0.26 [s, 9 H, CSi(C*H*$_3$)$_3$], 0.33 [s, 9 H, NSi(C*H*$_3$)$_3$], 1.63–2.02 (m, 15 H, Ad), 4.5 (s, 1 H, CH); ^{13}C-NMR (C$_7$D$_8$): δ 1.0 [CSi(*C*H$_3$)$_3$], 5.3 [NSi(*C*H$_3$)$_3$]; 29.6, 37.1, 42.4, 43.3 (Ad), 94.8 (*C*HSiMe$_3$), 185.7 [*C*(Ad)NSiMe$_3$]; ^{7}Li-NMR (C$_7$D$_8$): δ −1.20 and −1.39; ^{29}Si NMR (C$_7$D$_8$): δ −14.8 and −14.4 (C*Si*Me$_3$), −0.7 (N*Si*Me$_3$). MS (*M* denotes the parent) *m*/*z* (assignments, %): 321 ([*M*/2 - (Li + H)]$^+$, 20%).

[Li{μ,κ^2-N(SiMe$_3$)C(Ad)C(H)C(Ph)NSiMe$_3$}]$_2$ (2). Benzonitrile (0.40 cm^3, 3.92 mmol) was added dropwise to a solution of **1** (1.30 g, 1.98 mmol) in diethyl ether (25 cm^3) at 0 °C. The yellow mixture was stirred at 20 °C for *ca.* 16 h. Volatiles were removed *in vacuo* leaving a residual yellow powder. Yellow crystals of **2** (1.50, 89%) (found: C, 69.1; H, 9.21; N, 6.56. C$_{50}$H$_{78}$Li$_2$N$_4$Si$_4$ requires C, 69.7; H, 9.13; N, 6.50%), mp 155–160 °C were obtained from a hot hexane solution by cooling to −18 °C. ^{1}H-NMR: δ 0.12 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ph)], 0.48 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ad)]; 1.68, 2.01 (2 broad s, 15 H, Ad), 5.90 (s, 1 H, CH), 7.13–7.45 (m, 5 H, C$_6$H$_5$); ^{13}C-NMR: δ 2.9 [(*C*H$_3$)$_3$SiNC(Ph)], 4.9 [(*C*H$_3$)$_3$SiNC(Ad)]; 29.6, 37.1, 41.9, 44.1 (Ad), 108.0 (CH), 127.2–149.3 (C$_6$H$_5$), 178.0 (N*C*Ph), 184.0 (N*C*Ad); ^{7}Li-NMR: δ 0.18; ^{29}Si-NMR: δ −17.7 (Me$_3$SiNCPh), −4.4 (Me$_3$SiNCAd). MS (*M* denotes the parent) *m*/*z* (assignments, %): 289 ([*M*/2 - (Ad + H)]$^+$, 100%).

[Li{μ,κ^2-N(SiMe$_3$)C(Ad)C(H)C(C$_6$H$_4$Me-4)NSiMe$_3$}]$_2$ (3). As for **2**, from 4-MeC$_6$H$_4$CN (0.70 cm^3, 5.86 mmol) and **1** (1.90 cm^3, 2.90 mmol) in diethyl ether (35 cm^3) there were obtained X-ray quality yellow crystals of **3** (1.46, 57%) (found: C, 69.7; H, 9.41; N, 6.53. C$_{52}$H$_{82}$Li$_2$N$_4$Si$_4$ requires C, 70.2; H, 9.30; N, 6.30%), mp 135–140 °C. ^{1}H-NMR: δ 0.15 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ph)], 0.49 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ad)]; 1.67, 1.99 (2 broad s, 15 H, Ad), 2.06 (s, 3 H, C*H*$_3$-C$_6$H$_4$), 5.98 (s, 1 H, CH), 6.93–7.32 (m, 4 H, C$_6$H$_4$); ^{13}C-NMR: δ 2.7 [(*C*H$_3$)$_3$SiNC(Ph)], 4.8 [(*C*H$_3$)$_3$SiNC(Ad)], 21.1 (*C*H$_3$-C$_6$H$_4$); 29.6, 37.1, 41.7, 44.0 (Ad), 109.2 (CH); 126.7, 128.8, 137.7, 145.5 (C$_6$H$_4$), 181.3 (N*C*Ph), 186.7 (N*C*Ad); ^{7}Li-NMR: δ 0.16; ^{29}Si-NMR: δ −15.7 (Me$_3$SiNCPh), −1.9 (Me$_3$SiNCAd). MS (*M* denotes the parent) *m*/*z* (assignments, %): 303 ([*M*/2 - (Ad + H)]$^+$, 100%).

[Al{κ^2-N(SiMe$_3$)C(Ad)C(H)C(Ph)NSiMe$_3$}Me$_2$] (4). A one molar solution of chloro(dimethyl)alane in hexanes (0.72 cm^3, 0.72 mmol) was added dropwise to a suspension of **2** (0.31 g, 0.36 mmol) in hexane (20 cm^3) at 0 °C, then stirred at 0 °C for 30 min and set aside at 20 °C for *ca.* 16 h. The mixture was filtered. Evaporation of volatiles *in vacuo* from the filtrate furnished a yellow solid, which was freed from volatiles *in vacuo* yielding the yellow powder **4** (0.32, 92%). Yellow, X-ray quality crystals were isolated by cooling a concentrated pentane solution of **4** at −18 °C. ^{1}H-NMR: δ −0.13 [s, 6 H, (CH$_3$)$_2$Al], 0.04 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ph)], 0.47 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ad)], 1.50–1.92 (m, 15 H, Ad), 6.03 (s, 1 H, CH), 6.94–7.15 (m, 5 H, C$_6$H$_5$); ^{13}C-NMR: δ −5.8 [(CH$_3$)$_2$Al], 2.7 [(*C*H$_3$)$_3$SiNC(Ph)], 6.0 [(*C*H$_3$)$_3$SiNC(Ad)], 29.1, 36.6, 41.5, 44.7 (Ad), 112.8 (CH), 127.0–144.7 (C$_6$H$_5$), 180.6 (N*C*Ph), 192.5 (N*C*Ad); ^{27}Al-NMR: δ 154.5 (Δν$_{1/2}$ ∼ 5 KHz); ^{29}Si-NMR: δ −0.62 (Me$_3$SiNCPh), 8.43 (Me$_3$SiNCAd).

[Al{η^3-N(SiMe$_3$)C(Ad)C(H)SiMe$_3$}{κ^1-N(SiMe$_3$)C(Ad)=C(H)-SiMe$_3$-*E*}Me] (5). A one molar solution of dichloro(methyl)alane in hexanes (2.20 cm^3, 2.20 mmol) was

added dropwise to a solution of **1** (1.44 g, 2.2 mmol) in hexane (50 cm^3) at 0 °C, then stirred at 20 °C for *ca.* 16 h. The mixture was filtered. Evaporation of volatiles *in vacuo* from the filtrate afforded an off-white solid, which upon crystallisation from pentane at −18 °C produced colourless crystals of **5** (1.00, 66%) (found: C, 63.7 (duplicate analysis); H, 10.60; N, 4.15. $C_{37}H_{71}AlN_2Si_4$ requires C, 65.0; H, 10.47; N, 4.10%), mp 120–125 °C. ^{1}H-NMR: δ −0.13 [s, 2.6 H, (C*H*$_3$)Al]; 0.19, 0.26, 0.32 and 0.38 [bs, 36 H, (C*H*$_3$)$_3$SiNC(Ad)], 1.69 (bs, 15 H, Ad), 1.96 (bs, 15 H, Ad), 4.83 (bs, 1 H, CH); ^{13}C-NMR: δ 2.1 [(CH$_3$)$_2$Al], 3.5, 4.0, 4.2 and 4.5 [(*C*H$_3$)$_3$SiNC(Ad)], 28.3, 29.2, 36.0, 36.9, 38.5, 40.9, 41.8, 43.9 and 44.7 (Ad), 115.3 (*C*H), 137.2 (N(R)*C*(Ad)=C(H)R), 174.9 (N*C*Ph), 192.5 (N(R)*C*(Ad)C(H)R); ^{27}Al-NMR: δ 127.3 ($\Delta\nu_{1/2}$ ∼ 4.2 KHz); ^{29}Si-NMR: δ −10.27 (Me$_3$SiC(H)), 5.19 and 6.05 (Me$_3$SiNCAd). MS (*M* denotes the parent) *m*/*z* (assignments, %): 651 ([*M* - 2 Me]$^+$, 40%), 531 ([*M* - Me - Ad]$^+$, 60%), 186 (100%).

[Al{κ^2-N(SiMe$_3$)C(Ph)C(H)C(Ad)NSiMe$_3$}{κ^1-N(SiMe$_3$)C(Ad)=C(H)SiMe$_3$-*E*}Me] (6). Benzonitrile (1.00 cm^3, 0.98 mmol) was added dropwise to a solution of **5** (0.65 g, 0.95 mmol) in hexane (12 cm^3) at 0 °C. The mixture was set aside at 20 °C for *ca.* 16 h. Removal of volatiles *in vacuo* yielded the yellow powder **6** (0.62 g, 80%) (found: C, 65.7; H, 9.50; N, 5.57. $C_{44}H_{76}AlN_3Si_4$ requires C, 67.2; H, 9.68; N, 5.35%), mp 170–172 °C. Yellow X-ray quality crystals were obtained by crystallisation from Et_2O at 20 °C. ^{1}H-NMR: δ 0.09 (s, 3 H, CH_3Al), 0.14 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ph)], 0.37 [s, 9 H, (C*H*$_3$)$_3$SiC(H)], 0.45 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ad)], 0.46 [s, 9 H, (C*H*$_3$)$_3$SiNC(Ad)], 1.56–2.19 (m, 30 H, Ad), 5.31 (s, 1 H, C*H*$_{enamide}$), 6.10 (s, 1 H, C*H*$_{diket.}$), 6.95–7.12 (m, 5 H, C_6H_5); ^{13}C-NMR: δ −0.7 (CH_3Al), 3.2 [(*C*H$_3$)$_3$SiNC(Ph)], 4.3 [(*C*H$_3$)$_3$SiCH], 5.7 [(*C*H$_3$)$_3$SiNC(Ad)], 6.5 [(*C*H$_3$)$_3$SiNC(Ad)]; 29.1, 29.7, 36.7, 37.1, 41.4, 42.7, 44.8 (Ad), 116.6 (CH), 119.3 (CH), 127.5–143.3 (C_6H_5), 174.5 (N*C*Ph), 183.0 (N*C*Ad$_{enamine}$), 189.5 (N*C*Ad$_{diket.}$); ^{27}Al-NMR: δ 124 ($\Delta\nu_{1/2}$ ∼ 5.4 KHz); ^{29}Si-NMR: δ -−14.72 [Me$_3$SiC(H)], −5.17 (Me$_3$SiNCAd$_{enamide}$), −0.84 (Me$_3$SiNCPh), 8.52 (Me$_3$SiNCAd$_{diket.}$). MS (*M* denotes the parent) *m*/*z* (assignments, %): 770 ([*M* - (Me + H)]$^+$, 3%), 465 ([*M* - {RNC(Ad)C(H)R} - H]$^+$, 100%).

[Sn{η^3-N(SiMe$_3$)C(Ad)C(H)SiMe$_3$}$_2$] (7). The homoleptic bis(trimethylsilyl)amidotin(II) compound (0.53 g, 1.20 mmol) in hexane (20 cm^3) was added to a suspension of **1** (0.79 g, 1.20 mmol) in hexane (40 cm^3) at 20 °C. The resultant yellow solution was set aside for *ca.* 16 h at 20 °C. Partial removal of volatiles *in vacuo* yielded yellow crystals of **7** (0.83 g, 90%) (found: C, 56.3; H, 9.08; N, 3.86. $C_{36}H_{68}N_2Si_4Sn$ requires C, 56.9; H, 9.02; N, 3.68%), mp 154–156 °C. ^{1}H-NMR (C_7D_8): δ 0.23, 0.28, 0.30 [s, 18 H, Si(CH$_3$)$_3$], 0.46 [s, 10 H, Si(CH$_3$)$_3$], 1.62 and 1.74 (bs, 13 H, Ad), 1.88–1.95 (m, 12 H, Ad), 2.73 [s, 1.4 H, C(*H*)R], 4.65 [s, 0.4 H, C(*H*)R]; ^{13}C-NMR (C_7D_8): δ 0.6, 1.6, 2.1, 2.6 and 4.7 [(*C*H$_3$)$_3$Si], 29.1, 36.9, 40.6, 41.5, 45.4, 46.6 (Ad); ^{29}Si NMR (C_7D_8): δ −11.8, −11.5, 1.05 and 2.3; ^{119}Sn-NMR (C_7D_8): δ −377.3. MS (*M* denotes the parent, *L* denotes the ligand) *m*/*z* (assignments, %): 760 ([*M*]$^+$, 75%), 692 (15%), 572 (40%), 440 ([*M*–*L*]$^+$, 75%), 321 ([*L*+ H]$^+$, 55%), 306 ([*L* + H - Me]$^+$, 50%), 217 ([*L* + H-2Me]$^+$, 50%), 186 ([*L* + 2 H–Ad]$^+$, 50%).

[Li(N{C(Ad)=C(H)SiMe$_3$}{Si((NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2)SiMe$_3$})(thf)$_2$] (8). The azaallyllithium compound **1** (0.48 g, 0.73 mmol)

Table 5 Crystal data and refinement for the compounds **1** and **3–8**

	1	**3**	**4**	**5**	**6**	**7**	**8**[a]
Formula	$C_{36}H_{68}Li_2N_2Si_4$	$C_{52}H_{82}Li_2N_4Si_4\cdot(C_6H_{14})$	$C_{27}H_{45}AlN_2Si_2$	$C_{36.9}H_{70.7}AlCl_{0.1}N_2Si_4$	$C_{44}H_{76}AlN_3Si_4$	$C_{36}H_{68}N_2Si_4Sn$	$C_{42}H_{76}LiN_3O_2Si_3$
M	655.16	975.63	480.81	685.6	786.42	759.97	746.27
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$ (No.14)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	*Pbca* (No. 61)	*Pbca* (No. 61)	$Pna2_1$ (No. 33)
a/Å	17.9148(5)	10.5486(5)	6.5294(2)	11.3363(4)	11.9220(2)	16.1969(3)	19.3106(7)
b/Å	12.7201(3)	11.7160(5)	12.4764(4)	12.5576(4)	19.0977(3)	23.3707(5)	18.0975(4)
c/Å	19.5483(5)	13.3180(7)	17.8535(4)	17.0946(6)	41.4159(7)	22.0743(3)	13.1943(5)
α/°	90	70.084(3)	97.866(2)	70.347(2)	90	90	90
β/°	115.991(1)	87.413(4)	93.585(2)	89.000(2)	90	90	90
γ/°	90	74.873(4)	98.304(2)	65.500(2)	90	90	90
U/Å^3	4003.8(2)	1492.14(12)	1420.58(8)	2064.2(1)	9429.7(3)	8355.8(3)	4611.1(3)
Z	4	1	2	2	8	8	4
Abs. coeff./mm^{-1}	0.17	0.14	1.12	0.20	0.18	0.75	0.14
Unique reflections, $R_{int.}$	9493, 0.049	4109, 0.047	8060, 0.037	9759, 0.039	8303, 0.088	9857, 0.046	7935, 0.040
Reflections with $I > 2\sigma(I)$	7317	3348	6885	7956	5601	7747	7322
Final *R* indices for [$I > 2\sigma(I)$] R_1, wR_2	0.050, 0.126	0.057, 0.169	0.044, 0.111	0.048, 0.116	0.055, 0.126	0.033, 0.073	0.038, 0.092
R indices (all data) R_1, wR_2	0.071, 0.135	0.071, 0.184	0.054, 0.118	0.063, 0.126	0.093, 0.141	0.049, 0.080	0.043, 0.096

[a] The Flack parameter for **8** is −0.07(8).

in thf (15 cm^3) was added dropwise to the benzo-1,2-di(neopentylamino)silylene (**IX**) (0.40 g, 1.46 mmol) in thf (20 cm^3) at −30 °C. Volatiles were removed *in vacuo* yielding a cream solid (1.13 g) which was dissolved in hot hexane (5 cm^3) and afforded upon cooling white crystals of **8** (0.99, 90%) (found: C, 66.7; H, 10.11; N, 6.13. $C_{42}H_{76}LiN_3O_2Si_3$ requires C, 67.6; H, 10.26; N, 5.63%), mp 119–121 °C. ^{1}H-NMR: δ 0.08 and 0.18 (two s, [*E*-**8**]H), 0.31 and 0.47 (two s, *Z*-**8**), 0.41 and 0.52 (two s, *E*-**8**) (together 18 H, $SiMe_3$); 1.08 (s, H[**8**]), 1.17 (s, *E*-**8**) and 1.32 (s, *Z*-**8**) (together 18 H, Bu^t); 1.26 (br s, 8 H, thf); 1.52–2.12 (br multiplets, 15 H, Ad), 3.56 (br s, 8 H, thf), 3.08–3.47 (3 AB systems partly overlapped with thf, 4 H, CH_2Bu^t); 4.02 (br s, NH of H[**8**]); 4.04, 4.13 and 4.29 [s, 1 H, C=C(*H*)$SiMe_3$]; 6.7, 6.8 and 6.9 (multiplets, 4 H, C_6H_4); ^{13}C-NMR: δ 0.5, 2.7 and 4.8 ($SiMe_3$), 25.1 (thf), 29.7, 29.0, 34.4, 36.9, 37.7, 41.8, 42.9, 57.1, 68.3 (thf), 94.9, 108.2, 109.6, 116.7, 117.8 and 143.8 (C_6H_4), 177.9 (*C*=CHR); ^{7}Li-NMR: δ 0.76 and 0.18; ^{29}Si-NMR (inverse gated): δ −9.9, −12.6, −14.9, −17.3, −18.1, −22.0, −24.7, −27.4, −37.4. MS (*M* denotes the parent) *m*/*z* (assignments, %): 595 ([*M*–Li-2 thf]$^+$, 60), 580 ([*M*–Li - 2 thf - MeH]$^+$, 50), 522 ([*M*–Li-2 thf - $SiMe_3$]$^+$, 45), 347 ([*M*–Li-2 thf -{NNp}$_2C_6H_4$-1,2)]$^+$, 20).

Crystal data and refinement details for 1 and 3–8†

Diffraction data for each compound were collected on an Enraf-Nonius Kappa-CCD diffractometer, using monochromated Mo Kα radiation, λ 0.71073 Å. Crystals were directly mounted on the diffractometer under a stream of cold nitrogen gas. For **3**, the hexane solvate was disordered across an inversion centre; it was included with its C atoms (the terminal C atom was not located) having a common isotropic displacement parameter, the H atoms were omitted: 1,2-C–C distances were restrained to be equal, as were 1,3 C···C distances. For **6**, there was disorder of the substituent at Al: 90% methyl at C37 and 10% with a Cl atom in that position; the disorder was not resolved. Absorption correction was applied for **7** only. The structures were refined on all F^2 using SHELXL-97.[20] Further details are given in Table 5. Illustrations of structures are shown using ORTEP-3 for Windows.

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