Novel α,ω-bis(trialkylsilyl)-allyl and -1-azapentadienyl ligands; structures of [Li{η^3-CH(CHSiMe$_2$Bu^t)$_2$}(tmen)], [Li{N(SiMe$_3$)CBu^t(CH)$_3$SiMe$_2$Bu^t}(tmen)] and [K{η^4-N(SiMe$_2$Bu^t)CBu^t(CH)$_3$SiMe$_2$Bu^t}]$_\infty$†

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The η^3-allyl–lithium or –potassium compounds [Li{η^3-CH(CHSiMe$_2$Bu^t)(CHSiMe$_2$R)}(tmen)] (R = Bu^t 3a, Me 3b) and K{η^3-CH(CHSiMe$_2$Bu^t)$_2$} (obtained from Bu^{t}Me$_2$SiCH$_2$CH=CHSiMe$_2$R) with Bu^{t}CN afford the 1-azapentadienyl–lithium or –potassium compounds [Li{η^1-N(SiMe$_2$R)C(Bu^t)(CH)$_3$SiMe$_2$Bu^t}L] (L = tmen, R = Bu^t 6a, Me 6b; L absent, R = Bu^t 8a, Me 8b) or [K{η^4-N(SiMe$_2$Bu^t)C(Bu^t)(CH)$_3$SiMe$_2$Bu^t}]$_\infty$ 7.

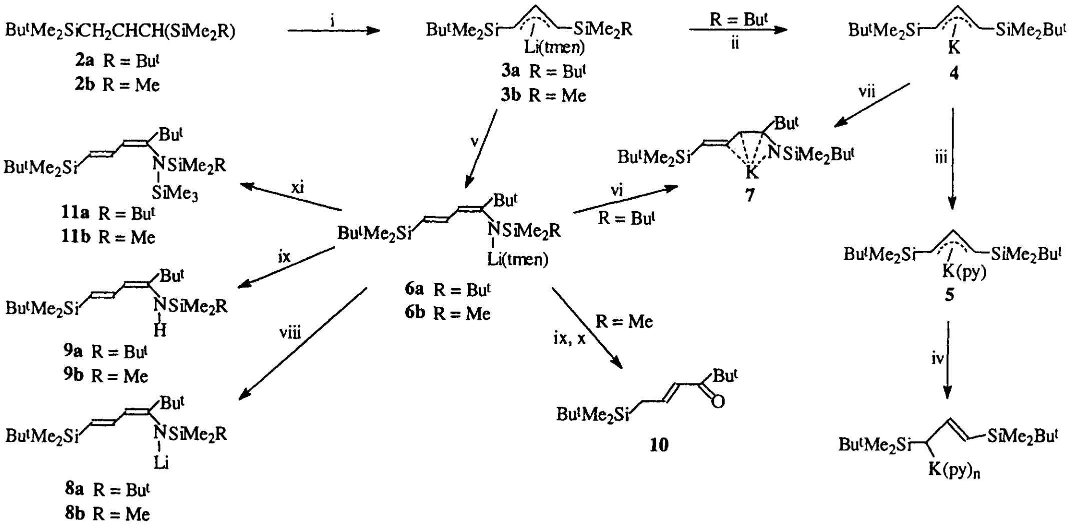
We report the synthesis, structures and some reactions of the lithium or potassium derivatives of some novel ligands, which we believe may prove to be of general interest in organometallic and coordination chemistry. These ligands are α,ω-bis-[dimethyl(alkyl)silyl]-allyls and -1-azapentadienyls; one example of the former was known, the X-ray-authenticated [Li{η^3-CH(CHSiMe$_3$)$_2$}(tmen)] [tmen = Me$_2$N(CH$_2$)$_2$NMe$_2$].[1]

Treatment of allylmagnesium bromide with Bu^{t}Me$_2$SiF in Et$_2$O yielded Bu^{t}Me$_2$SiCH$_2$CH=CH$_2$ **1**. From **1** or the known SiMe$_3$ analogue, and successively LiBu^t(tmen) and Bu^{t}Me$_2$SiF in n-C$_6$H$_{14}$, there was obtained Bu^{t}Me$_2$SiCH$_2$CH=CH(SiMe$_2$R) (R = Bu^t **2a**, Me **2b**); which with LiBu^n(tmen) yielded [Li{η^3-CH(CHSiMe$_2$Bu^t)(CHSiMe$_2$R)}(tmen)] (R = Bu^t **3a**, Me **3b**) (i in Scheme 1).

The allyllithium compound **3a** with KOBu^t afforded K{η^3-CH(CHSiMe$_2$Bu^t)$_2$} **4**, which with pyridine (py) gave K{η^3-CH(CHSiMe$_2$Bu^t)$_2$}(py) **5**; **5** in C$_5$D$_5$N was shown by NMR spectroscopy to be a σ-allyl complex K{C(SiMe$_2$Bu^t)CH=CHSiMe$_2$Bu^t}(py)$_n$ (ii–iv in Scheme 1). Treatment of the bis(silyl)allyllithium complex, **3a** or **b** with Bu^{t}CN yielded the 1-azapentadienyllithium complex [Li{N(SiMe$_2$R)C(Bu^t)(CH)$_3$SiMe$_2$Bu^t}(tmen)] (R = Bu^t **6a**, Me **6b**) (v in Scheme 1). The polymeric compound [K{η^4-N(SiMe$_2$Bu^t)C(Bu^t)(CH)$_3$SiMe$_2$Bu^t}]$_\infty$ **7** was prepared either from **4** + Bu^{t}CN or **6a** and KOBu^t (vi or vii in Scheme 1). The tmen-free analogues **8a,b** or **6a,b** were obtained from the latter by successively controlled hydrolysis and lithiation; hydrolysis alone gave the secondary dieneamines NH(SiMe$_2$R)C(Bu^t)(CH)$_3$SiMe$_2$Bu^t (R = Bu^t **9a**, Me **9b**) (viii and ix, in Scheme 1). Attempts to purify **9a,b** by chromatography through an alumina column were successful for **9a**, but **9b** yielded (x in Scheme 1) the α,β-unsaturated ketone Bu^{t}C(O)(CH)$_2$CH$_2$SiMe$_2$Bu^t **10** (perhaps as a result of hydrolysis of **9b**, leading initially to the primary dieneamine). Reaction of **6a** or **6b** with Me$_3$SiCl (xi in Scheme 1) gave the tertiary dieneamine N(SiMe$_3$)(SiMe$_2$R)C(Bu^t)(CH)$_3$SiMe$_2$Bu^t (R = Bu^t **11a**, Me **11b**).

Reaction v, whereby **3a,b** with Bu^{t}CN gave **6a,b** evidently involved not only C–C coupling but also a 1,3-silicotropic C → N migration; an analogous rearrangement was observed in the LiCH(SiMe$_3$)$_2$–Bu^{t}CN system, yielding the 1-azaallyllithium compound [Li{CH(SiMe$_3$)C(Bu^t)NSiMe$_3$]$_2$.[2] It is interesting that for the **3b** → **6b** transformation, the migrating group was exclusively SiMe$_3$; the isomer Li{N(SiMe$_2$Bu^t)C(Bu^t)(CH)$_3$SiMe$_3$}(tmen) of **6b** was not detected.

Both the hydrolysis and trimethylsilylation of the dieneamidolithium compound **6a,b** (reactions ix and xi, respectively) showed them to behave as N-centred nucleophiles, whereas such reactions of metallated enamines generally afford the



Scheme 1 Synthesis of the bis(trialkylsilyl)allyl and 1-azapentadienyl–lithium and –potassium complexes **3–8** and some of their reactions. *Reagents and conditions*: i, LiBu(tmen), hexane, −78 °C to room temp., 12 h; ii, KOBu^t, hexane, room temp., 4 h; iii, pyridine, hexane; iv, pyridine; v, Bu^{t}CN, R = Bu^t, THF, reflux, 9 h; R = Me, Et$_2$O or THF, room temp., 12 h; vi, KOBu^t, hexane, room temp., 4 h; vii, Bu^{t}CN, THF, 75–80 °C, 6 h; viii, H$_2$O, THF, room temp., 30 min then LiBu, hexane, room temp., 1 h and reflux 5 h; ix, H$_2$O, THF, room temp., 30 min; x, alumina column chromatography; xi, Me$_3$SiCl, hexane, room temp., 3 h and reflux 2 h.

C-protonated or -silylated tautomers. Secondary enamines often exist in equilibrium with their imine tautomers,[3] but for toluene solutions of each of the dieneamines **9a**,**b** there was no evidence (^{1}H NMR spectroscopy)‡ of the presence of the imine $RMe_2SiN{=}C(Bu^t)CH_2(CH)_2SiMe_2Bu^t$ in the range 25–80 °C. The dominance of the dieneamines is probably attributable to their greater conjugative stabilisation. *cis–trans* Isomerism is, in principle, possible for **9a**,**b**, but NMR spectra showed each to be a single compound, assigned to have the structure shown in Scheme 1, both for steric reasons and by analogy with the X-ray data for **6b** and **7**.

Each of the compounds **1–11** gave satisfactory microanalytical, as well as ^{1}H, ^{13}C, ^{7}Li (**3**, **6**, **8**) and ^{29}Si (**3**, **5**, **6**) NMR,‡ IR (**9–11**) and GC-MS (**9–11**) spectra. Additionally, single-crystal X-ray diffraction data established the molecular structures of complexes **3a**, **6b** and **7** (Fig. 1);§ the structures of **3a** and **6b** will be presented in a full paper.

The lithium atom in the crystalline allyllithium complex **3a** lies almost symmetrically above the allyl group, with the metal-to-central carbon [C(2)] bond distance slightly shorter than Li–C(1) or Li–C(3), as is usual for η^3-metal complexes.[4] Comparison with $[Li\{\eta^3\text{-}CH(CHSiMe_3)_2\}(tmen)]$[1] shows that **3a** has the more symmetrical structure.

Crystalline complex **6b** is a mononuclear buta-1,3-dienylamidolithium compound, rather than an η^5-1-azapentadienyllithium. The Li–N(1) [N(1) being the amido nitrogen] distance of 1.910(8) Å is a little short for a mononuclear four-coordinate lithium amide, which generally fall within the range 1.94–2.01 Å;[5] another mononuclear three-coordinate lithium amide is $Li\{N(SiMe_3)_2\}(tmen)$. Both the amido nitrogen and the lithium atom are in a trigonal-planar environment, the sum of the angles at N(1) and Li being 358.5 and 359.6°, respectively.

The crystalline potassium complex **7**, by contrast to the lithium complex **6b**, is a polymer, Fig. 1. Each anion is related to two K^+ cations on crystallographic inversion centres. The potassium ions lie above and below η^4-1-azapentadienyl anions, the K–C distances being in the range 2.945(4)–3.562(4) Å for C(1) to C(3), that to C(1) being the shortest and to C(3) the longest. This may be compared with the mean $K–C(Si)_3$ bond lengths of 3.09 Å in $[K\{C(SiMe_3)_3\}]_\infty$, in which each potassium is also in close contact with six methyl groups, ranging from 3.16(2) to 3.31(1) Å.[6] The mean K–N distances of 2.92 Å in **7** are comparable to the 2.84 Å in $[K\{\eta^3\text{-}N(R)C(Ar)NC(Ar)CHR\}L]_\infty$ (R = $SiMe_3$, Ar = $C_6H_3Me_2$-2,5; L = NCAr).[7]

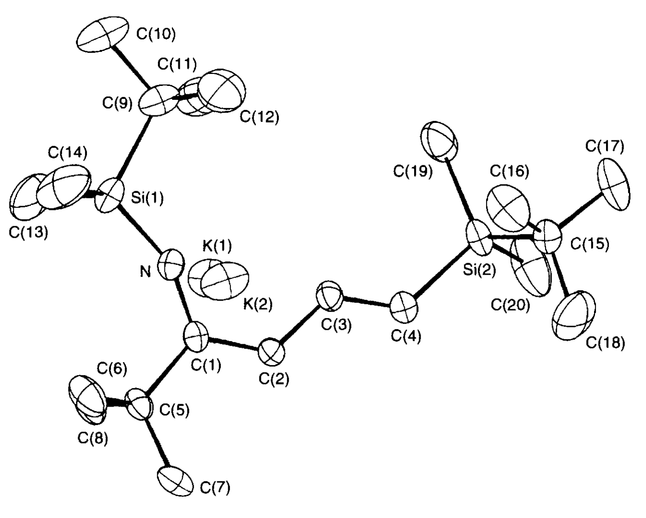


Fig. 1 ORTEP representation of a 1-azapentadienyl anion in relation to two neighbouring potassium cations in crystalline **7**. Selected bond lengths (Å): K(1)–N 2.954(3), K(2)–N 2878(3), K(1)–C(1) 3.017(4), K(2)–C(1) 2.945(4), K(1)–C(2) 3.183(4), K(2)–C(2) 3.248(4), K(1)–C(3) 3.343(4), K(2)–C(3) 3.562(4).

Three examples of 1-azapentadienylmetal complexes have been published: $[Mn\{N(R)C(Me)C(H)C(H)CH_2\}(CO)_3]$ (R = Pr^i, Bu^t),[8] believed (NMR) to have the ligand in an η^5- bonding mode, and the X-ray-characterised $[Ir\{N(Bu^t)C(H)C(H)C(H)CH_2\text{-}3,4,5,\text{-}\eta^3\text{-}syn\}(PMe_3)_3]$;[9] see also ref. 10. A dilithium 3-azapentadienyl complex $[Li(tmen)]_2[NC_5H_3\{CH(SiMe_3)_2\}\text{-}2,6]$ is also of interest.[11]

Among the experiments in progress on the new ligands, transmetallations of **6a**,**b**, **7a**, **8a**,**b** feature prominently. Particularly noteworthy are the reactions of **6a** with $FeCl_2$ and $CoCl_2$, which have provided the first thermally stable diallyls of iron(II) and cobalt(II).

We thank the Chinese Government and the British Council for the award of a studentship to Z.-X. W. and the EPSRC for other support.

Footnote

† No reprints available.

‡ *Selected NMR data* [^{1}H 360.1, ^{13}C{^{1}H} 62.9, ^{7}Li{^{1}H} 97.2, ^{29}Si{^{1}H} 49.7 MHz; 293 K; C_6D_6]. **3a**: ^{1}H δ 0.14 (s, 6 H, $SiMe_2$), 0.29 (s, 6 H, $SiMe_2$), 1.22 (s, 18 H, Bu^t), 1.59 (s, 4 H, NCH_2), 1.81 (s, 12 H, NMe), 2.83 (d, 2 H, CH), 7.04 (t, 1 H, CH); ^{13}C{^{1}H} δ −4.21, −2.58 (SiMe), 18.62 (*C*Me_3), 27.46 (C*Me*$_3$), 46.15 (NMe), 56.56 (NCH_2), 64.53, 156.52 (3 CH); ^{7}Li{^{1}H} δ −0.22; ^{29}Si{^{1}H} δ −3.20. **6b**: ^{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, NCH_2), 1.80 (S, 12 H, NME), 5.52 (D, 1 H, CH), 5.93 (D, 1 H, CH), 7.40 (dd, 1 H, CH); ^{13}C{^{1}H} δ −4.56 ($SIME_2$), 4.71 ($SIME_3$), 17.37 (*C*Me_3), 27. 20 (C*Me*$_3$), 30.31 (C*Me*$_3$), 39.07 (*C*Me_3), 45.17 (NMe), 56.04 (NCH_2), 107.21, 109.68, 149.65 (3 CH), 171.80 (171.80 (NC); ^{7}Li{^{1}H} δ −0.07; ^{29}Si{^{1}H} δ −19.32, −0.09.

§ *Crystal data*: **7a**, $C_{20}H_{42}KNSi_2$; M = 391.8, triclinic, space group $P\bar{1}$ (no. 2), a = 11.142(2), b = 11.189(2), c = 12.208(2) Å, α = 73.73(1), β = 63.70(1), γ = 69.44(1)°, U = 1263.4(4) Å^3, $F(000)$ = 432; Z = 2, D_c = 1.03 g cm^{-3}, μ(Mo-Kα) = 3.1 cm^{-1}, specimen 0.35 × 0.30 × 0.20 mm, 4440 independent reflections for $2 < \theta < 25°$, 2615 reflections with $[|F^2| > 2\sigma(F^2)]$; $R1$ = 0.063, $wR2$ = 0.240 (for all data).

Intensities were measured to θ_{max} 25° on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation (λ = 0.71069 Å); no absorption correction. Structure refinements were by SHELXL-93, and H atoms at fixed positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/132.

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Received, 22nd March 1996; Com. 6/02006B