Lithium(η^3-aza-allyl) Type Complexes derived from the Metallation of $2\text{-}(Me_3Si)_{3-n}CH_nC_5H_4N$; Influence of Solvent and Degree of Substitution, $n = 1$ or 2, on the Nature of the Product

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Metallation of $2\text{-}(Me_3Si)_2CHC_5H_4N$ (= R*H*) with $LiBu^n$ in hexane yields RLi · RH, (**1**), whereas RH with $LiBu^n$ and tmeda (tetramethylethylenediamine; 1 equiv.) in hexane affords RLi(tmeda), (**2**); the related $2\text{-}(Me_3Si)CH_2C_5H_4N$ (=R′*H*) with $LiBu^n$ in a hexane–diethyl ether mixture gives $[\{LiR'(OEt_2)\}_2]$, (**3**): compounds (**1**)—(**3**), shown by *X*-ray crystallography to have novel η^3-aza-allyl ligand geometries, are regarded as models for the bonding in the products of metallation of systems $CH_3\text{–}C(R'')\text{=}NR'''$.

Previously, we reported that the metallation of $2\text{-}(Me_3Si)_2CHC_5H_4N$ (= R*H*) using $LiBu^n$ in a hexane–diethyl ether mixture yielded a binuclear complex $(RLi)_2$, (**4**), (Scheme 1) in which the ligands bridged the lithium centres in an 8-membered ring structure.[1] We now report the structures of three further products of metallation of RH and of the related $2\text{-}(Me_3Si)CH_2C_5H_4N$ (= R′*H*) using $LiBu^n$ in hexane in the presence or absence of tmeda (tetramethylethylenediamine) or diethyl ether. These three products, compounds (**1**)—(**3**),† the preparative conditions for which are given in Scheme 1,

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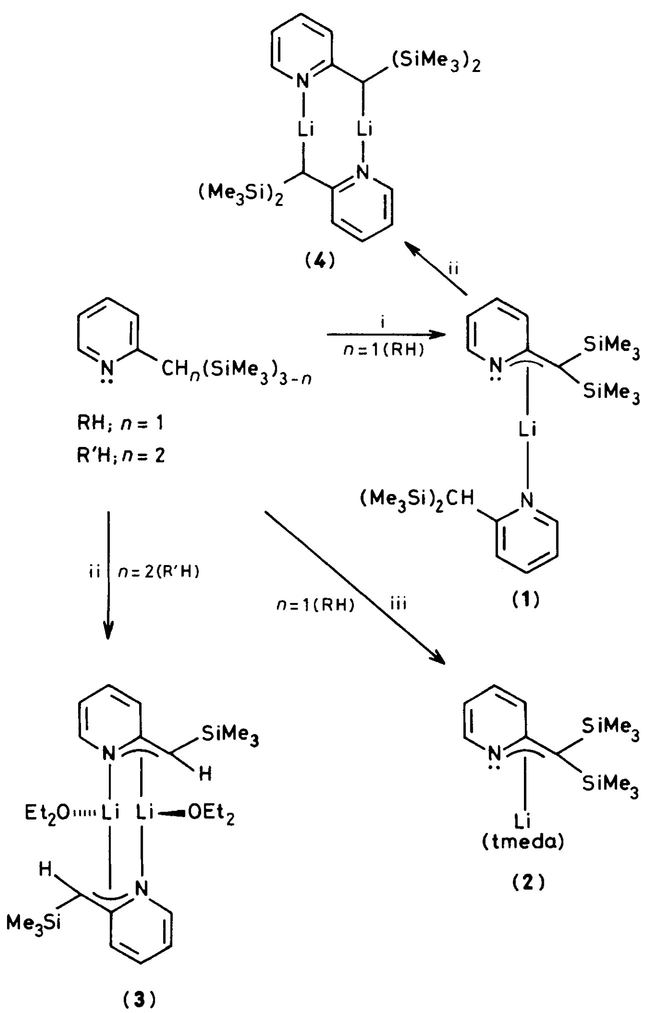
† The new compounds (**1**) (m.p. 123 °C), (**2**) (m.p. 83—85 °C), and (**3**) (m.p. 88—90 °C) prepared in *ca.* 80% yield have also been characterized by ^1H and ^{13}C n.m.r. spectroscopy.



Scheme 1. *Reagents and conditions:* i, LiBu^n (*ca.* 1.6 M in hexane); ii, as for i + OEt$_2$; iii, as for i + tmeda.

contain unprecedented η^3-aza-allyl ligand geometries. Key bond distances and angles are shown in Figures 1—3.‡

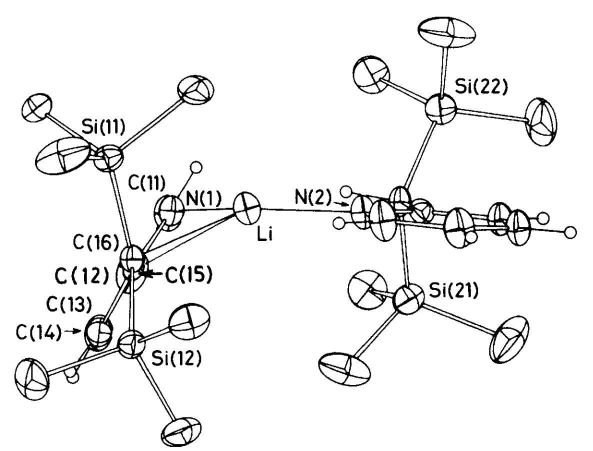


Figure 1. Molecular structure of (**1**) showing 20% thermal ellipsoids for the non-hydrogen atoms; the projection is onto the pyridine plane of the anionic ligand. Important distances and angles defining the lithium environment are Li–N(1) 2.00(1), Li–N(2) 2.01(1), Li–C(15) 2.32(1), Li–C(16) 2.22(1) Å, N(2)–Li–N(1), C(15,16) 142.1(6), 150.6(5), 142.0(5), N(1)–Li–C(15,16) 36.2(2), 68.9(3), C(15)–Li–C(16) 36.6(3)°.

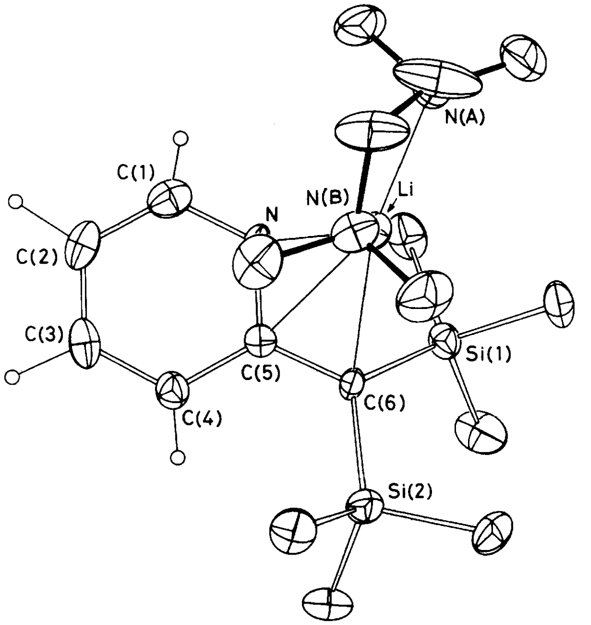


Figure 2. Molecular structure of (**2**) showing 20% thermal ellipsoids for the non-hydrogen atoms; the projection is normal to the pyridine plane. Important distances and angles defining the lithium environment are Li–N 1.96(2), Li–C(5) 2.46(2), Li–C(6) 2.43(2), Li–N(A) 2.17(2), Li–N(B) 2.06(2) Å, N(A)–Li–N(B), N, C(5,6) 86.4(7), 116.8(9), 150.0(9), 154.5(9), N(B)–Li–N, C(5,6) 116.6(9), 111.6(8), 116.4(8), N–Li–C(5,6) 34.0(4), 64.8(5), C(5)–Li–C(6) 33.6(4)°.

The Li–C distances of the Li-η^3-C$_2$N group differ significantly for the three compounds, ranging from 2.22 to 2.46 Å. However they are within the limits established for compounds with the well known Li-η^3-C$_3$ fragment, *e.g.*, 2.19—2.63(1) Å in [{Li(tmeda)}$_2${(2-Me$_3$SiCHC$_6$H$_4$)$_2$}]^2 and 2.21—2.58(2) Å in Li{N(CH$_2$CH$_2$)$_3$N}{CH$_2$C$_6$H$_5$}.^{3} In (**1**) and (**3**) each lithium atom is approximately coplanar with an aromatic ring plane (Figure 1) with which it is bound by the nitrogen atom, possibly with some π bonding, at a short distance of 2.01(1) (**1**), 2.04(1) Å (**3**) [*cf.*, 1.936(4) Å (**4**)].^{1} The Li–O bond distance of 1.91(2) Å in (**3**) is short, *cf.*, 1.943(6) in [{Li{μ-N(SiMe$_3$)$_2$}OEt$_2$}$_2$]^4 and 2.094(4)—2.393(3) Å in

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‡ *Crystal data:* Compound (**1**) C$_{24}$H$_{45}$LiN$_2$Si$_4$, M = 480.9, triclinic, space group $P\bar{1}$, a = 16.707(6), b = 10.553(4), c = 9.044(3) Å, α = 86.67(3), β = 78.35(3), γ = 86.13(3)°, U = 1556(1) Å^3, D_c = 1.03 g cm^{-3} (Z = 2), F(000) = 524.

Compound (**2**), C$_{18}$H$_{38}$LiN$_3$Si$_2$, M = 359.6, monoclinic, space group $P2_1/c$, a = 9.606(4), b = 15.036(7), c = 16.60(1) Å, β = 97.40(3)°, U = 2378(2) Å^3, D_c = 1.00 g cm^{-3} (Z = 4), F(000) = 792.

Compound (**3**), C$_{13}$H$_{24}$LiNOSi, M = 245.4, triclinic, space group $P\bar{1}$, a = 10.88(2), b = 10.58(2), c = 8.24(1) Å, α = 73.5(1), β = 85.2(1), γ = 63.1(1)°, U = 810(2) Å^3, D_c = 1.01 g cm^{-3} (Z = 2), F(000) = 268.

The structures were determined at 295 K, from 3076 [(**1**)], 1515 [(**2**)], and 1071 [(**3**)] observed reflections [$I > 3\sigma(I)$] out of a total of 3824, 3125, and 2093 respectively (Mo-K_α radiation). R and R' values are 0.053 and 0.058 [(**1**)], 0.068 and 0.085 [(**2**)], and 0.056 and 0.062 [(**3**)]. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

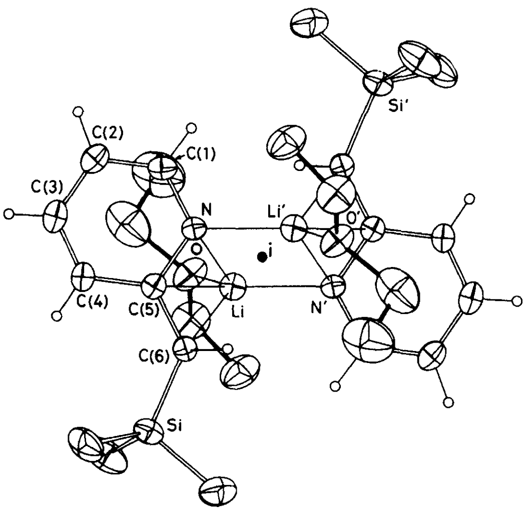

Figure 3. Molecular structure of (**3**) showing 20% thermal ellipsoids for the non-hydrogen atoms; the projection is normal to the pyridine plane. Important distances and angles defining the lithium environment are Li–N 2.19(1), Li–C(5) 2.34(1), Li–C(6) 2.36(1), Li–N′ 2.04(1), Li–O 1.91(1), Li · · · Li′ 2.64(1) Å, O–Li–N, C(5,6), N′ 116.7(6), 110.0(5), 122.7(4), 126.3(4), N–Li–C(5,6), N′ 35.6(2), 63.6(3), 103.0(4), C(5)–Li–C(6), N′ 34.6(3), 123.1(4), C(6)–Li–N′ 106.4(4)°.

$[Li\{N(SiMe_3)_2\}\{12\text{-crown-}4\}]$.[5] In (**1**) and (**2**) the trigonal plane of C(6) is skewed relative to the pyridine plane by 40.9 and 38.2°, respectively. This is minimal in (**3**) in which the silicon of the unique *exo*-$SiMe_3$ group resides only 0.07 Å out of the aromatic plane. The C(5)–C(6) distances of 1.428(8), (**1**) (anionic ligand), 1.42(1), (**2**), and 1.40(1) Å, (**3**), in contrast to 1.500(8) Å for the analogous distance of the neutral ligand in (**1**), suggest some C(5)–C(6) double bond character and substantial delocalization of charge.

Compounds (**1**)—(**3**) illustrate a lithium-η^3-aza-allyl type of interaction that may be general for the products of metallation of species $CH_3\text{–}CR''\text{=}NR'''$, usually represented in the literature[6,7] as $LiCH_2CR''\text{=}NR'''$ or $Li^+[CH_2{\cdots}CR''{\cdots}NR''']^-$. Their differences reflect the important roles played by Lewis base sites,[8] whether in solvent or substrate, and steric hindrance in organo-lithium chemistry, a theme that will be elaborated when the present results are discussed in full.

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