Lithiation of 2-$Me_3SiCHRC_5H_4N$(R = H or $SiMe_3$): Influence of Solvent on the Nature of the Product (from *X*-Ray Structure Determinations)† and Asymmetric Induction. A Note on the Lithiation of Some Analogous 3- and 4-Methylpyridines

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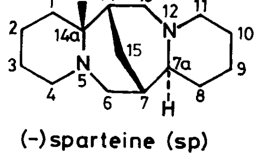
Metallation of 2-$Me_3SiCHRC_5H_4N$ (R = H or $SiMe_3$) using $LiBu^n$ in hexane, and in the presence of diethyl ether, and the ditertiary amines tmen (*N,N,N′,N′*-tetramethylethylenediamine) or sp [(−)sparteine] yields crystalline lithium complexes. These have been characterized using *X*-ray diffraction data for [Li{2-C($SiMe_3$)$_2$$C_5H_4N$}{2-CH($SiMe_3$)$_2$$C_5H_4N$}] (**1**), [{Li[2-C($SiMe_3$)$_2$$C_5H_4N$]}$_2$] (**2**), [Li(tmen){2-C($SiMe_3$)$_2$$C_5H_4N$}] (**3**), [{Li($OEt_2$)[2-CH($SiMe_3$)$C_5H_4N$]}$_2$] (**4**), [{Li(tmen)-[2-CH($SiMe_3$)C_5H_4N]}$_2$] (**5**), and [Li(sp){2-CH($SiMe_3$)C_5H_4N}] (**6**). In (**1**), (**3**), (**4**), and (**6**) the hydrocarbyl group acts as an η^3-aza-allyl through the ring nitrogen [2.00(1), 1.96(2), 2.19(1), and 1.985(6) Å], *ipso*-carbon [2.22(1), 2.43(2), 2.356(9), and 2.323(6) Å], and adjacent ring carbon [2.32(1), 2.46(2), 2.34(1), and 2.353(6) Å]; in (**4**) the nitrogen centre also bridges to another metal centre [2.041(1) Å]. Complex (**2**) has two co-ordinated lithium centres, each lithium bound by the *ipso*-carbon [2.213(7) Å] and a nitrogen centre from a centrosymmetric ligand [1.936(6) Å] and is thus an alkylmetal species; it can be recrystallized from tetrahydrofuran even though the lithiums are co-ordinatively unsaturated. In complex (**5**), the anionic ligand acts as an amide bridging two metal centres through the ring N [Li–N 2.08(1), 2.25(1) Å, N–Li–N 103.6(7), 93.0(9)°]. Treating (**6**) with MeI in hexane at −78 °C yields 2-[(1-trimethylsilyl)ethyl]pyridine of 20% estimated optical purity. The isomeric complex [Li(sp){4-CH($SiMe_3$)C_5H_4N}] under the same conditions gave no asymmetric induction; other metallations of 4-$Me_3SiCH_2C_5H_4N$, and some of 3-$Me_3SiCH_2C_5H_4N$ are also reported.

Alkyl-lithium reagents such as $LiBu^n$ are used extensively as metallating agents[1] with the site of metallation usually in accordance with predictions based on thermodynamic acidities. The structures of the products (degree of aggregation and covalency, and lithium to hydrocarbyl group connectivities), however, are usually complex and depend on the choice of solvent, and steric and electronic effects including those arising from functional groups within the organic substrate.[2] It is not surprising, therefore, that their structures are often oversimplified. For example, the metallation of 2-methylpyridine and related methylated heterocyclic compounds,[3] and imines,[4] yield species either formulated as alkyl-lithiums (Li–CH_2R), anionic species with the charge on the metallated carbon centre to emphasize the site of electrophilic attack in subsequent reactions, or as complexes with a π system in the anion arising from sp^2 overlap of the *ipso*-carbon centre and the adjacent multiple bond(s).

In general, organolithium species can associate in hydrocarbon solvents and some donor solvents such as ethers and monodentate and bidentate tertiary amines yielding structures with multicentre interactions. Monomeric species are found when lithium is in the preferred four-fold co-ordination environment, such as in complexes involving the tridentate tertiary amine *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdien),[5,6] and when solvated by thf (tetrahydrofuran) in solution.[7] Moreover, the number of lithium to hydrocarbyl group contacts can range from two in alkyl-lithium complexes to six in contact ion-pair structures involving conjugated anions.[2,8]



(−)sparteine (sp)

Herein, we report the results of a systematic study of the metallation of the trimethylsilylmethyl-substituted pyridines 2-(Me_3Si)CHRC$_5$H$_4$N, R = H or $SiMe_3$, using $LiBu^n$ in hexane, and in the presence of a variety of Lewis bases, diethyl ether, and the ditertiary amines tmen (*N,N,N′,N′*-tetramethylethylenediamine) or (−)sparteine.

While tmen has been used extensively in the lithiation of arylmethanes[9] the use of sparteine has been limited to a few studies with emphasis on asymmetric metallation,[3,10,11] which is an interest in the present study. Where possible all compounds have been structurally characterized using *X*-ray diffraction data. We also report some results on the metallation of analogous isomeric 3- and 4-methylpyridines to ascertain the effect of having the nitrogen functionality adjacent or remote to the site of metallation in the asymmetric studies. Some preliminary results of the metallations and details of the

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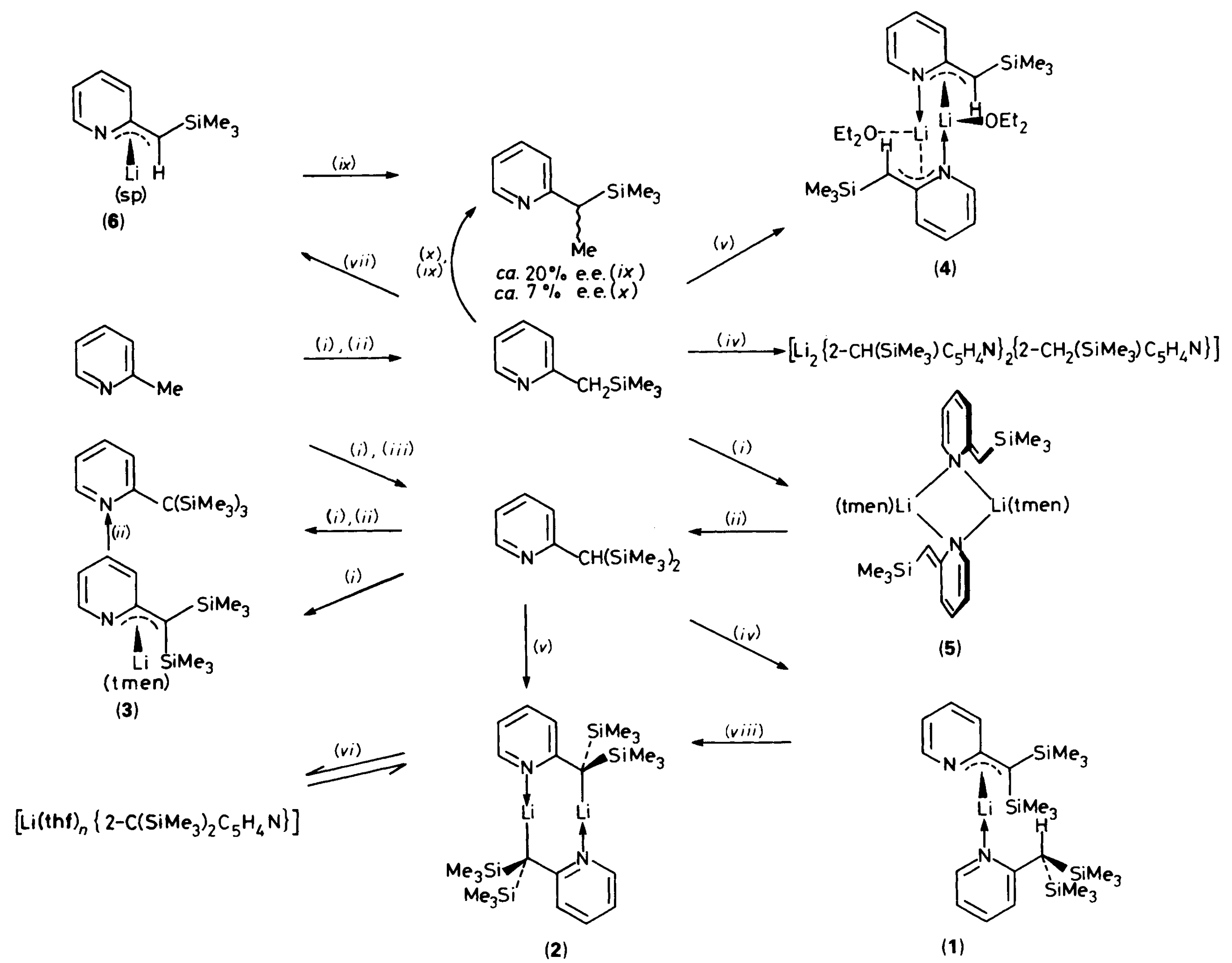
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: mmHg = 133 Pa.



Scheme 1. Reagents and conditions: (*i*) [Li(tmen)Bu^n], hexane, *ca.* 0 °C; (*ii*) $SiMe_3Cl$, hexane, *ca.* 20 °C; (*iii*) $SiMe_3Cl$, OEt_2, *ca.* 35 °C; (*iv*) $LiBu^n$, hexane, *ca.* 0 °C; (*v*) $LiBu^n$, hexane-OEt_2, *ca.* 20 °C; (*vi*) thf, *ca.* 20 °C; (*vii*) [Li(sp)Bu^n], hexane–OEt_2, *ca.* 20 °C; (*viii*) (*iv*) then *ca.* 0.2 mol equiv. of OEt_2; (*ix*) MeI, hexane, −78 °C; and (*x*) $MgBu^nBu^s$, heptane–OEt_2, *ca.* 20 °C then MeI in hexane, −95 °C

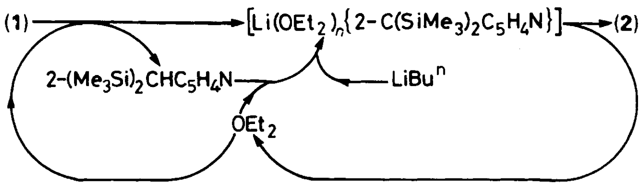
structures of the derived complexes, namely $[\{Li[2\text{-}C(SiMe_3)_2C_5H_4N]\}_2]$, $[Li\{2\text{-}C(SiMe_3)_2C_5H_4N\}\{2\text{-}CH(SiMe_3)_2C_5H_4N\}]$, $[\{Li(tmen)[2\text{-}C(SiMe_3)_2C_5H_4N]\}_2]$, and $[\{Li(OEt_2)[2\text{-}CH(SiMe_3)C_5H_4N]\}_2]$,[12] have been reported. Except for the first, η^3-aza-allyl bonding of the anion to the metal centre was established and it was proposed that this type of bonding could be regarded as a model for bonding in lithiated imines. Since then structures of a number of such complexes have been reported,[13–15] some with η^3-aza-allyl bonding.[13,14]

It is noteworthy that some of the solids encountered are useful transfer reagents of $2\text{-}(Me_3Si)CRC_5H_4N^-$ (R = H or $SiMe_3$) for main-group[16,17] and transition[16,18] metals. Related to the present study is the structure of monolithiated 2,6-dimethylpyridine, $[\{Li(tmen)(2\text{-}CH_2C_5H_3NMe\text{-}6)\}_2]$,[19] and its use in the synthesis of alkyl complexes of Hf and Th,[20] and the synthesis and structure of $[\{Li(tmen)\}_2\{2,6\text{-}(Me_3SiCH)_2C_5H_3N\}]$.[21] We note that metallation of 2-methylpyridine[22–24] and 2-trimethylsilylmethylpyridine[25] have previously been reported by other researchers but the organolithium complexes were not isolated.

Results and Discussion

Compounds $2\text{-}Me_3SiCHRC_5H_4N$ (R = H or $SiMe_3$) were prepared by the treatment of 2-methylpyridine with Li(tmen)Bu^n then $SiMe_3Cl$ under different conditions, yields *ca.* 80%, Scheme 1. When the orange powder of the intermediate organolithium reagent, assumed to be $[Li(tmen)(2\text{-}CH_2C_5H_4N)]$, is taken up in diethyl ether and added to an excess of $SiMe_3Cl$ in diethyl ether at *ca.* 30 °C the major product is $2\text{-}Me_3SiCH_2C_5H_4N$, whereas if $SiMe_3Cl$ is added to a hexane slurry of the same reagent at room temperature $2\text{-}(Me_3Si)_2CHC_5H_4N$ is the predominant product. This difference can be readily explained by noting that the relative acidities of the methyl groups in 2-methylpyridine and $2\text{-}Me_3SiCH_2C_5H_4N$, *i.e.* Me < CH_2SiMe_3, would favour metallation of preformed $2\text{-}Me_3SiCH_2C_5H_4N$ by unreacted $[Li(tmen)(2\text{-}CH_2C_5H_4N)]$, yielding 2-methylpyridine and $[\{Li(tmen)[2\text{-}CH(SiMe_3)C_5H_4N]\}_2]$; reaction of the latter with $SiMe_3Cl$ should then yield $2\text{-}(Me_3Si)_2CHC_5H_4N$. The above conditions for formation of the latter compound dictate that the supply of $SiMe_3Cl$ is continuously depleted, thus favouring the reaction of $2\text{-}Me_3SiCH_2C_5H_4N$ with unreacted $[Li(tmen)(2\text{-}CH_2C_5H_4N)]$. No tris(trimethylsilyl) substituted compound, $2\text{-}(Me_3Si)_3CC_5H_4N$, was isolated from the reaction mixtures even though the carbon bearing the trimethylsilyl group in $2\text{-}(Me_3Si)_2CHC_5H_4N$ is expected to be more acidic than the corresponding group in $2\text{-}Me_3SiCH_2C_5H_4N$ and 2-methylpyridine and thus more readily metallated.

Both compounds $2\text{-}Me_3SiCHRC_5H_4N$ (R = H or $SiMe_3$) have been prepared previously by the treatment of 2-methylpyridine with KNH_2 then excess of $SiMe_3Cl$, albeit in only 7



Scheme 2.

and 13% yield respectively,[26] and in high yield by metallation of 2-methylpyridine with LiNPr$^i_2$ in thf at −75 °C, followed by SiMe$_3$;[27] the use of LiNPr$^i_2$ is emerging as the most reliable method for lithiating methylated aromatic N-heterocyclic compounds to circumvent ring-addition reactions (see below).[28] Such addition is not a problem for 2-methylpyridine using [Li(tmen)Bu^n] as the metallating agent, but is when using LiBu^n in thf.[29]

Reactions of 2-Me$_3$SiCHRC$_5$H$_4$N (R = H or SiMe$_3$) with $\approx$1.6 mol dm^{-3} LiBu^n in hexane are summarized in Scheme 1. All the lithium complexes were isolated as highly air-sensitive crystalline solids and characterized by ^{1}H, ^{13}C, and ^{7}Li n.m.r. spectroscopy, and formation of derivatives by treatment with SiMe$_3$Cl and MeI; for most, crystal structure determinations were undertaken. Compound 2-Me$_3$SiCH$_2$C$_5$H$_4$N has previously been deprotonated by LiNPr$^i_2$ in thf at −78 °C.[30]

The mechanism of metallation in all cases presumably involves heteroatom-facilitated lithiation,[31] with the nitrogen centre increasing the nucleophilic character of Bu^n and directing LiBu^n into the neighbourhood of the active hydrogen. This has been established for selective metallations of methylated pyridines[3] and is *o*-tertiary amine substituent-directed for aryllithiations.[32,33]

Proton n.m.r. spectra show a dramatic upfield shift for the ring protons in metallated 2-Me$_3$SiCHRC$_5$H$_4$N, consistent with data for a number of deprotonated methyl-substituted pyridines,[34] being attributed to delocalization of charge. ^{13}C N.m.r. data show the signals corresponding to the carbon bearing SiMe$_3$ to be downfield relative to 2-Me$_3$SiCHRC$_5$H$_4$N, consistent with greater *p* character, although any negative charge on the *ipso*-carbon would have an opposite effect.

Metallation of 2-(Me$_3$Si)$_2$CHC$_5$H$_4$N.—In the absence of a Lewis base to activate the LiBu^n a 1:1 metallated:unreacted monomeric complex resulted [Li{2-C(SiMe$_3$)$_2$C$_5$H$_4$N}{2-CH(SiMe$_3$)$_2$C$_5$H$_4$N}] (**1**), with the neutral ligand bound through N and the anionic ligand bound in an η^3-aza-allyl manner to formally electron-deficient lithium (*X*-ray structure determination). The presence of an unreacted metal-bound substituted pyridine may have mechanistic implications. If complexation of 2-(Me$_3$Si)$_2$CHC$_5$H$_4$N to lithium is the primary process then it could facilitate the metallation of another ligand molecule by decreasing the degree of association of LiBu^n and increasing the nucleophilic character of the lithium reagent.[1] Quenching compound (**1**) with SiMe$_3$Cl afforded a 1:1 mixture of the ligand and 2-(Me$_3$Si)$_3$CC$_5$H$_4$N. The neutral ligand in (**1**) is resistant to lithiation in hexane even under more forcing conditions, higher temperature, *ca.* 30 °C for several hours, and a three-fold excess of LiBu^n. This implies it is non-labile and that the bulky trimethylsilyl groups and N-complexed lithium shield the proton attached to the carbon bearing two trimethylsilyl groups. Addition of a small amount of diethyl ether (*ca.* 0.2 equiv.) in a mixture of (**1**) and excess of LiBu^n catalyses the formation of the novel, pale yellow, dimeric complex [{Li[2-C(SiMe$_3$)$_2$C$_5$H$_4$N]}$_2$] (**2**) (*X*-ray structure), which is sublimable *in vacuo* with minimal decomposition and is devoid of diethyl ether even though the lithium centres are co-ordinatively unsaturated. It also lacks multicentre interactions usually associated with lithiums of this type,[1] for example in the diethyl etherate, [{(1-Li-8-Me$_2$NC$_{10}$H$_6$)(OEt$_2$)}$_2$].[33] Buttressing effects of the bulky silyl groups presumably preclude the formation of solvated (**2**) and also multicentre bonding. The ability of silicon to concentrate charge on adjacent carbon centres by polarization may also be important.[35]

Complex (**2**) is also formed using diethyl ether as a solvent and interestingly can be recrystallized from thf, although ^{7}Li n.m.r. data suggest the integrity of the dimer is not maintained in thf solution; in benzene the chemical shift is 1.24 p.p.m., which is >1 p.p.m. downfield from other species in this study, reflecting the presence of low-co-ordinate lithium, and in thf the chemical shift is -1.12 p.p.m. The downfield chemical shift for anionic carbon centres discussed above is less pronounced in this compound which is commensurate with an *sp*^{3} anionic carbon; in all other structures in this study this carbon is approximately trigonal planar *sp*^{2} and the shifts are much larger.

The most likely species present in thf are monomers, [Li(thf)$_n${2-C(SiMe$_3$)$_2$C$_5$H$_4$N}] with $n = 2$, by analogy with the structure of the tmen adduct (see below). Solvation by thf in solution may have implications concerning the diethyl ether-catalysed formation of (**2**) from (**1**), *viz.* that there is co-ordination of diethyl ether to the electron-deficient centre in (**1**) allowing release of neutral ligand for metallation, followed by competitive complexation (oxygen *vs.* nitrogen centres), Scheme 2.

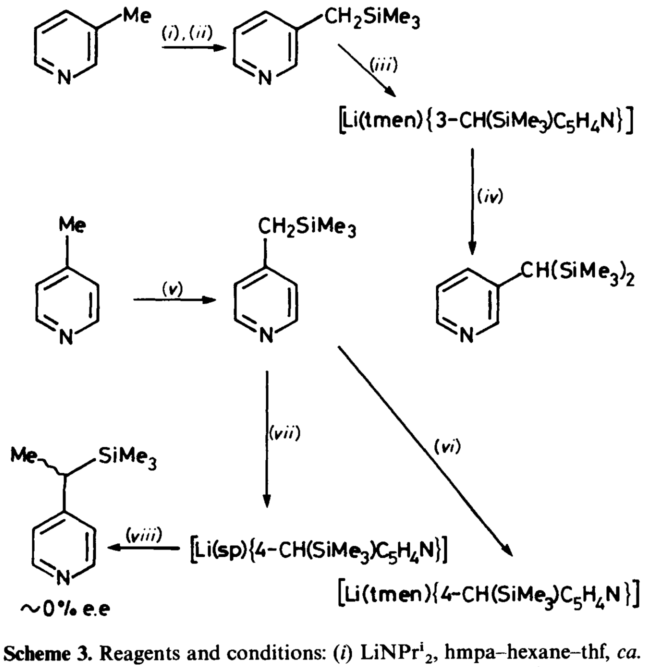
Metallation of 2-(Me$_3$Si)$_2$CHC$_5$H$_4$N using [Li(tmen)Bu^n] resulted in formation of [Li(tmen){2-C(SiMe$_3$)$_2$C$_5$H$_4$N}], as a deep red solid in which the hydrocarbyl group is bound as an η^3-aza-allyl group (*X*-ray structure), as in the structure of (**1**). In contrast to the foregoing thf-solvated species which crystallizes as the unsolvated dimer, there is no evidence for Lewis-base dissociation yielding (**2**). The chelate effect for tmen together with the metal centres now being co-ordinatively saturated should disfavour ligand dissociation and dimerization. A compound isolobal with 2-(Me$_3$Si)$_2$CHC$_5$H$_4$N, PhCH(SiMe$_3$)$_2$, fails to react with [Li(tmen)Bu^n] under the same conditions.[36] This suggests that in the present reaction there is intramolecular activation, as discussed above.

Metallation of 2-(Me$_3$Si)CH$_2$C$_5$H$_4$N.—n-Butyl-lithium in hexane gave a pale yellow solid of composition Li$_2$[2-CH(SiMe$_3$)C$_5$H$_4$N]$_2$[2-CH$_2$(SiMe$_3$)C$_5$H$_4$N] (n.m.r. spectroscopy); crystals were unsuitable for an *X*-ray structure determination. Addition of excess of LiBu^n failed to metallate the co-ordinated neutral ligand, as in (**1**). Subsequent addition of a small amount of diethyl ether (*ca.* 0.2 equiv.) resulted in formation of [{Li(OEt$_2$)[2-CH(SiMe$_3$)C$_5$H$_4$N]}$_2$] (**4**) and neutral ligand (isolated), in contrast to the above diethyl ether-catalysed conversion of (**1**) into (**2**). Seemingly lower steric hindrance about the *ipso*-carbon in 2-(Me$_3$Si)CHC$_5$H$_4$N$^-$ results in the ether being locked up in the product.

Lithiation in a hexane–diethyl ether mixture gave exclusively yellow crystals of dimeric (**4**), in which each ligand is acting as an η^3-aza-allyl to one lithium and an N-donor to the other (*X*-ray structure). This contrasts with the formation of an ether-free dimeric complex (**2**) from 2-(Me$_3$Si)$_2$CHC$_5$H$_4$N under the same conditions, in which the anion is acting as an alkyl/N-donor.

The compounds [Li(tmen)Bu^n] and [Li(sp)Bu^n] with 2-(Me$_3$Si)CH$_2$C$_5$H$_4$N yield different structural types in the solid state, respectively dimeric [{Li(tmen)[2-CH(SiMe$_3$)C$_5$H$_4$N]}$_2$], (**5**), and monomeric [Li(sp){2-CH(SiMe$_3$)C$_5$H$_4$N}], (**6**). In (**5**) the anionic group is behaving as a bridging amido ligand with an exocyclic double bond, although n.m.r. data are consistent with an η^3-aza-allyl interaction in solution; in (**6**) the anion is η^3-aza-allyl to one metal centre, as in the tmen adduct of Li[2-C(SiMe$_3$)$_2$C$_5$H$_4$N] (above).

Metallation using [Li(sp)Bu^n] is of interest in asymmetric



Scheme 3. Reagents and conditions: (*i*) LiNPr$^i_2$, hmpa–hexane–thf, *ca.* 20 °C; (*ii*) SiMe$_3$Cl, thf, *ca.* 0 °C; (*iii*) [Li(tmen)Bu^n], hexane, *ca.* −30 °C; (*iv*) SiMe$_3$Cl, *ca.* 0 °C; (*v*) LiNPr$^i_2$, hexane–thf, −78 °C; (*vi*) [Li(tmen)Bu^n], hexane, *ca.* 0 °C; (*vii*) [Li(sp)Bu^n], hexane–OEt$_2$, *ca.* 20 °C; (*viii*) MeI, hexane, −78 °C

induction (= enantiomeric excess, e.e.) and in this regard compound (**6**) was treated with MeI, yielding 2-[(1′-trimethylsilyl)ethyl]pyridine. Maximum induction under the conditions studied was estimated as 20%, using ^{1}H n.m.r. spectroscopy with a lanthanide chiral shift reagent, the optimum separation of peaks being achieved for 0.40 mol equiv. of tris[3-(perfluorobutyryl)bornan-2-onato]europium(III) at a concentration of 2-Me$_3$SiCHMeC$_5$H$_4$N of *ca.* 0.1 g cm^{-3} in CDCl$_3$. Metallation in diethyl ether, hexane, and benzene at 25 °C and quenching crystalline (**6**) with MeI in hexane at −95 °C gave respectively 20, 15, and 1% asymmetric induction. Quenching (**6**) formed in diethyl ether in hexane at 0 °C gave 7% induction, and in diethyl ether at −95 °C negligible induction. Thus the use of diethyl ether in the metallation step improves the asymmetric induction as does the use of hexane in the quenching step. Complex (**6**) rapidly precipitates when formed in hexane, whereas in diethyl ether it slowly crystallizes possibly allowing preferential formation of one of the diastereoisomers *via* equilibration involving solvent-separated ion pairs with co-ordinated solvent, (*R*)-(**6**) $\rightleftharpoons$ (*S*)-(**6**). In the quenching step in diethyl ether, formation of such solvent-separated ion pairs, which are expected to be more reactive, should result in loss of asymmetric induction. The ^{7}Li n.m.r. spectrum in toluene of a sample of (**6**) formed in diethyl ether gave a singlet, implying a rapid exchange process on the n.m.r. time-scale so that either there is no distinction between the two possible diastereoisomers, or the resonances for such isomers are isochronous.

In an attempt to improve the asymmetric induction the relatively new metallating reagent, MgBu^{n}Bu^s,[16] was investigated. Reaction of [Mg(sp)Bu^{n}Bu^s] with 2-(Me$_3$Si)CH$_2$C$_5$H$_4$N in hexane, then MeI under the optimum conditions for [Li(sp)Bu^n], however, gave only 7% asymmetric induction which could not be improved. Overall, the use of (-)sparteine to form optically active 2-substituted pyridines has met with limited success. In establishing the role, if any, of the aromatic nitrogen centre, adjacent to the site of metallation, in assisting the asymmetric induction, 3- and 4-substituted pyridines with the nitrogen centre remote from the metallation site were investigated (see below).

Metallation of 3-Me$_3$SiCH$_2$C$_5$H$_4$N.—This compound was prepared from 3-methylpyridine using LiNPr$^i_2$ in hmpa (hexamethylphosphoric acid triamide) according to the method of Kaiser and Petty[37] (Scheme 3), yield 55%. The use of [Li(tmen)Bu^n] gave only 7% yield; other methods for metallation of 3-methylpyridine also give poor yields. These include the use of LiBu^n in thf,[29] Group 1 metal amides in ammonia, LiNPr$^i_2$ and NaPh in benzene, and LiNPr$^i_2$ in diethyl ether.[38]

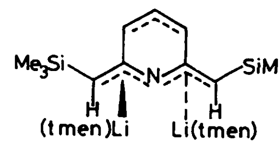
Metallation of 3-Me$_3$SiCH$_2$C$_5$H$_4$N using [Li(tmen)Bu^n] yielded an orange solid, [Li(tmen){3-CH(SiMe$_3$)C$_5$H$_4$N}] (n.m.r. spectroscopy) which afforded 3-(Me$_3$Si)$_2$CHC$_5$H$_4$N on quenching with SiMe$_3$Cl, although in low yield, *ca.* 15%. The compounds [Li(sp)Bu^n] and 3-Me$_3$SiCH$_2$C$_5$H$_4$N gave an oil which on treating with MeI afforded a mixture of ring-addition products, 74%, and 3-[(1′-trimethylsilyl)ethyl]pyridine, 15% (gas chromatography–mass spectrometry, g.c.–m.s.); these could not be separated and rapidly decomposed in air.

Metallation of 4-Me$_3$SiCH$_2$C$_5$H$_4$N.—This compound was prepared from 4-methylpyridine using LiNPr$^i_2$ in thf as the metallating agent followed by treatment of the reaction mixture with SiMe$_3$Cl, yield 80% (Scheme 3); [Li(tmen)Bu^n] in hexane gave a mixture of 4-(Me$_3$Si)$_2$CH$_2$C$_5$H$_4$N, 4-(Me$_3$Si)$_2$CHC$_5$H$_4$N, and addition products, 32:16:38 (g.c.–m.s.). The use of LiBu^n in the absence of tmen gives a high yield of the 1,2-addition product.[23,29]

Metallation of the neutral ligand with [Li(tmen)Bu^n] in hexane gave the expected product, [Li(tmen){4-CH(SiMe$_3$)C$_5$H$_4$N}]. Similarly [Li(sp)Bu^n] in hexane or diethyl ether gave [Li(sp){4-CH(SiMe$_3$)C$_5$H$_4$N}], and quenching with MeI under the same conditions for maximum asymmetric induction for the corresponding 2-substituted complex gave 4-[(1′-trimethylsilyl)ethyl]pyridine but with no asymmetric induction, Scheme 3. Therefore the nitrogen centre adjacent to the site of metallation in 2-(Me$_3$Si)CH$_2$C$_5$H$_4$N plays a key role in its asymmetric induction. This is possibly because of strong aromatic nitrogen complexation attenuating solvent-separated ion pairs and thus loss of chiral information at the *ipso*-carbon centre.

Structure Determinations.—Results of the crystal structure determinations of compounds (**1**)—(**6**) are given in Tables 1—7 and Figures 1—6. The compounds comprise discrete monomeric [(**1**), (**3**), and (**6**)] and dimeric species [(**2**), (**4**), and (**5**)]. The asymmetric unit in each case is the complete molecule [(**1**), (**3**), and (**6**)], or one half of the molecule [(**2**), (**4**), and (**5**)], the other half being generated by a centre of inversion [(**2**), and (**4**)] or a C_2 axis [(**5**)].

Structures based on 2-(Me$_3$Si)$_2$CC$_5$H$_4$N$^-$. In complexes (**1**) and (**3**) the anionic ligand acts in an η^3-aza-allyl manner through the nitrogen centre [2.00(1), (**1**); 1.96(2) Å, (**3**)], the *ipso*-carbon, C(6) [2.22(1), (**1**); 2.43(2) Å, (**3**)], and adjacent ring carbon, C(5) [2.32(1), (**1**); 2.46(2) Å, (**3**)], in a similar manner to that in, (**4**), (**6**), and (**7**)[21] (see below). That the Li–C distances are longer in (**3**) than in (**1**) is consistent with greater metal solvation in (**3**), *viz.* more electron density on the metal centre, resulting in weaker metal–ligand bonding. Despite an η^3-aza-allyl mode of interaction, the trigonal planes of C(6) in (**1**) and (**3**) are skewed relative to the pyridine plane by 40.9 and 38.2° respectively (Figures 1 and 3, and Figures 1 and 2 of ref. 12*b*), most likely a consequence of the bulk of the trimethylsilyl groups. Such a mode of interaction maximizes the occupancy of the metal co-ordination sphere while maintaining the metal in close proximity to the anionic *ipso*-carbon and nitrogen centres, with delocalization of charge from C(6) to the ring. In compounds (**4**), (**6**) and (**7**) with less congestion around the *ipso*-



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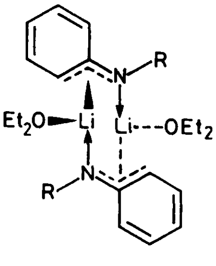
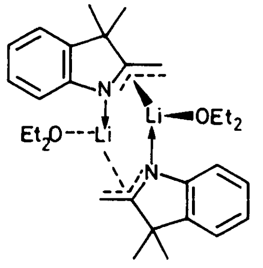
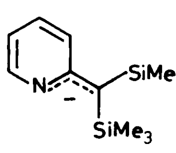


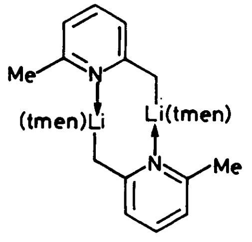
(8) R = C(CH$_2$)Bu^t



(9)



(10)



(11)

carbons, the Si–C–C angles, 130.1(4), 130.6(2), and 128.3°, are more open than for the anionic ligand in (**1**) and (**3**), 114.4(4), 120.9(6)° [Si(1)], and 121.5(4), 118.5(6)° [Si(2)]. In addition, the trigonal planes of the *ipso*-carbons are now coplanar with the aromatic planes. Lithium—η^3-aza-allyl interactions have been established for other systems, (**8**)[13] and (**9**),[14] and lithium polyhapto interactions involving nitrogen centres have also been established for lithiated hydrazones.[39] An alternative mode of interaction for 2-$(Me_3Si)_2CC_5H_4N$ in a monomeric species would be a stereochemically unfavourable four-membered chelate ring.

The presence of a neutral ligand, 2-$(Me_3Si)_2CHC_5H_4N$, in (**1**) co-ordinated through the nitrogen is useful for comparison of the geometry in the anionic ligand. The most significant differences are: (*i*) the angles about C(6) are enlarged in the anion; (*ii*) the C(4)–C(5) and N–C(5) distances, 1.431(8) and 1.376(7) Å, in the anion, which are similar to the corresponding distances in (**3**), 1.42(1) and 1.38(1) Å, are elongated relative to those in the neutral ligand 1.395(8) and 1.347(7) Å; (*iii*) a decrease in C(5)–C(6), 1.500(8) to 1.428(8) Å, which compares with 1.42(1) Å in (**3**), and (*iv*) the C(6)–Si distance (average) in the anion, 1.83$_8$ Å, which is similar to that in (**3**), 1.84$_0$ Å, is shorter than the corresponding distances in the neutral ligand, 1.88$_6$ Å, in accordance with the polarization by silicon of an anionic carbon centre.[35] Items (*ii*) and (*iii*) reflect the η^3-aza-allyl representation of bonding and delocalization of charge in the anion, which can best be represented as in (**10**). Inspection of Figure 1 (and Figure 1 of ref. 12*a*) shows that the 'active' H atom on the neutral ligand in (**1**) is directed towards the metal centre and is shielded by the two silyl groups of the same ligand, and also by the anionic ligand. Such shielding may account for the inability to abstract H using LiBu^n in the absence of an auxiliary Lewis base (see above).

The Li–C interactions in compound (**1**), (**3**), (**4**), (**6**), and (**7**)[21] are related to η^3-allyl systems where the *ipso*-carbon is attached to an aromatic ring devoid of a heteroatom, *e.g.* in $[\{Li(tmen)\}_2\{2\text{-}(Me_3Si)CHC_6H_4\}_2]$, 2.19—2.63(1) Å.[40] How-

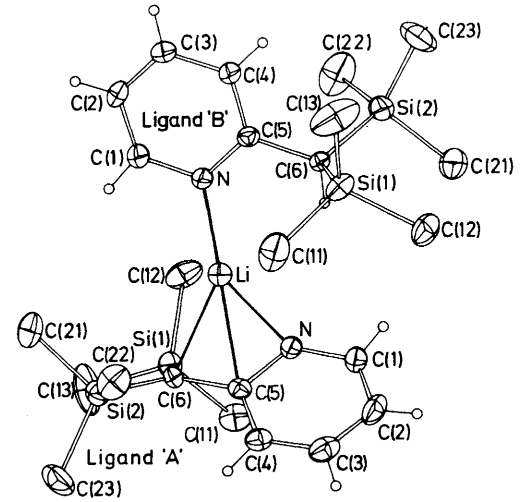


Figure 1. Molecular projection of compound (**1**), showing 20% thermal ellipsoids for non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å and for clarity have been omitted from the silyl groups. Atom labelling is shown

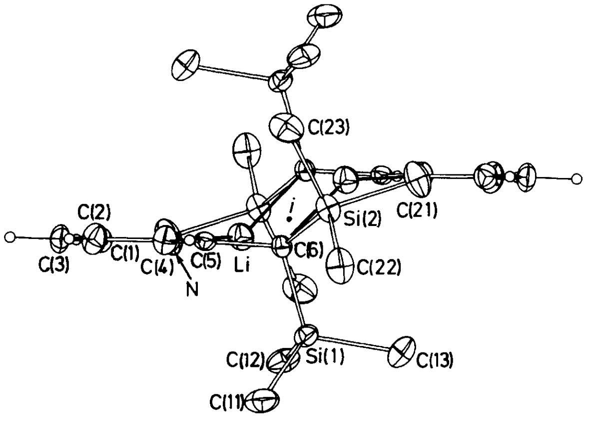


Figure 2. Molecular projection of compound (**2**), at right angles to the pyridine ring plane; a projection onto the pyridine ring planes is given in ref. 18

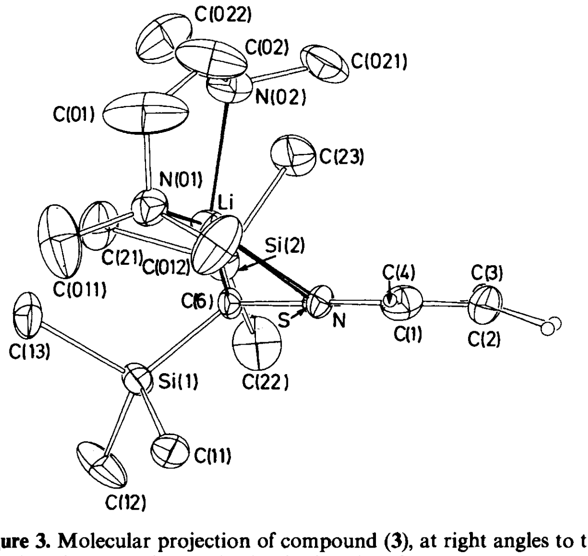


Figure 3. Molecular projection of compound (**3**), at right angles to the pyridine plane; another projection is given in ref. 19

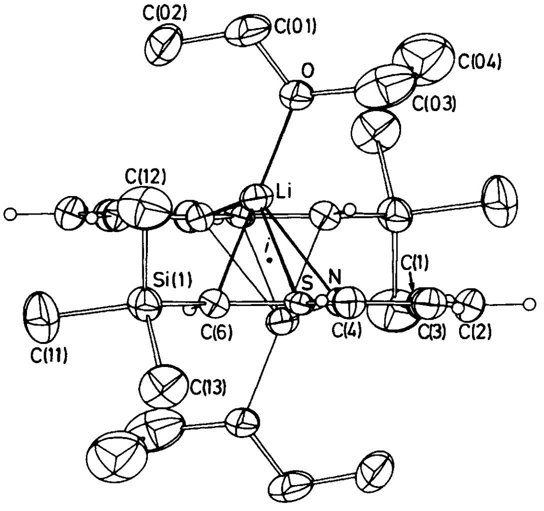


Figure 4. Molecular projection of compound (4); a projection onto the pyridine planes is given in ref. 19

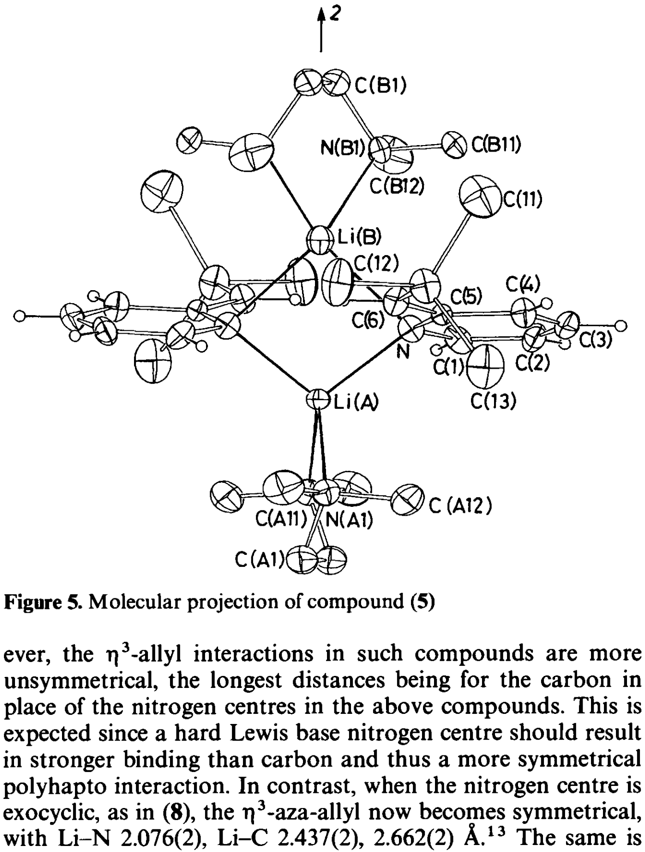


Figure 5. Molecular projection of compound (5)

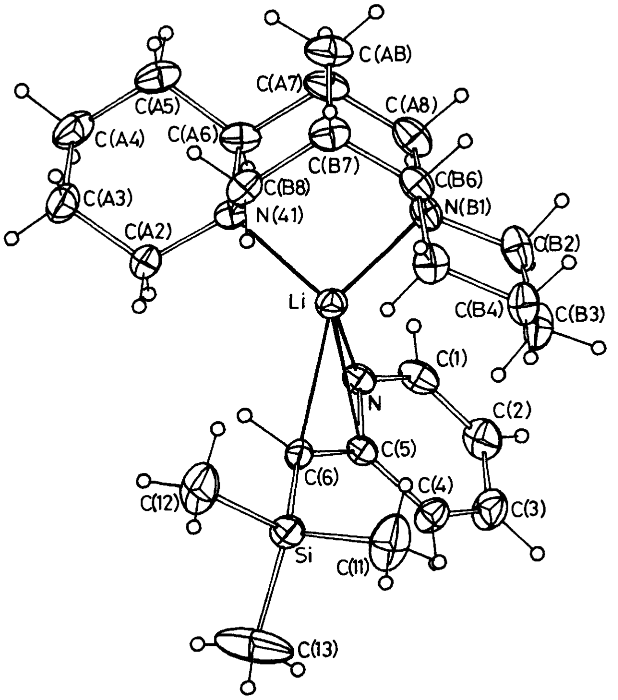


Figure 6. Molecular projection of compound (6)

ever, the η^3-allyl interactions in such compounds are more unsymmetrical, the longest distances being for the carbon in place of the nitrogen centres in the above compounds. This is expected since a hard Lewis base nitrogen centre should result in stronger binding than carbon and thus a more symmetrical polyhapto interaction. In contrast, when the nitrogen centre is exocyclic, as in (8), the η^3-aza-allyl now becomes symmetrical, with Li–N 2.076(2), Li–C 2.437(2), 2.662(2) Å.[13] The same is also found for the imine-derived η^3-aza-allyl (9), for which Li–N 2.090(6), Li–C 2.37, 2.51 Å.[14]

In compound (1) the lithium is coplanar with the aromatic ring of the neutral ligand [deviation 0.11 Å, *cf.* 1.11 Å from the anion in both (1) and (3)], at a distance of 2.01(1) Å from the nitrogen centre. This is rather short, suggesting σ- and π-type contributions to bonding, and compares with Li–N(aromatic) distances in other systems with co-ordinatively unsaturated lithium centres, for example 2.011(11) Å in [{Li(8-Me$_3$Si-NC$_9$H$_6$N)}$_2$].[41] The Li–N distances for tmen in (3), and also (4), are unexceptional.[40]

In compound (2) the anionic ligand bridges two lithium centres through C(6) and N forming an eight-membered ring, as in (11), although there the lithium centres have additional tmen ligands. Presumably the steric hindrance of the silyl groups in (3) precludes the formation of a binuclear species like (11). Each lithium atom in (2) is coplanar with its immediate pyridine ring, deviation 0.01 Å, but is 1.21(2) Å out of the inverse of the same plane so that the complex has a step structure (Figure 2, and Figure 1 of ref. 12*a*). It is unusual for an alkyl lithium species to be co-ordinatively unsaturated, yet devoid of multicentre bonding; the only other two-co-ordinate lithium is in the 'ate' complex [Li{C(SiMe$_3$)}$_2$]$^+$.[42] The stability of two-co-ordination arises from the steric hindrance of the silyl groups, and possibly also the electronic effect of the silyl groups, notably that the latter can stabilize negative charge on the *ipso*-carbon, C(6), by polarization, attenuating charge delocalization onto the ring and thus favouring σ bonding. However, other complexes containing 2-(Me$_3$Si)$_2$CC$_5$H$_4$N, and also 2-Me$_3$SiCHC$_5$H$_4$N, have η^3-aza-allyl linkages with delocalization of charge. The absence of delocalization in (2) is reflected in the C(5)–C(6) distance, 1.475(4) Å, much longer than for η^3-aza-allyls, 1.428(8) [(1)] and 1.42(1) Å[(3)].

The Li–C(6) length of 2.213(7) Å in compound (2) is similar to that in the 'ate' complex above, 2.16(1) and 2.20(1) Å;[42] the nearest Li···C contact is to C(5) at 2.613(7) Å. The Li–N length is one of the shortest for a neutral N-donor bound to lithium, being more akin to Li-anionic N distances,[40] again reflecting the low valency of the metal centres. Other noteworthy features of (2) are: (*a*) the lithium centres in close proximity, 2.560(9) Å, although longer than the shortest Li···Li distance yet observed, 2.34 Å in an organovinyl lithium species,[43] for which some···Li bonding interaction is considered; (*b*) the N–Li–C angle is low, 146.9(4)°, for two-co-ordination; and (*c*) the presence of seemingly agostic H atoms. There are three lithium–methyl hydrogen contacts, at 2.23, 2.31, and 2.20 ($-x$, $-y$, $-z$) Å, which is common for organolithium species, having recently been the subject of theoretical treatment.[44] Items (*b*) and (*c*) are related; repulsion between the lithium centres and the formation of L···H contacts resulting in reduction of the C–M–N angle may be the origin of a step structure; in the isolobal copper, silver, and gold complexes[18] the eight-membered rings are planar, the C–M–N angles are close to 180°, and there are no significant metal–hydrogen contacts.

Table 1. Non-hydrogen atom co-ordinates of compound (**1**)

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Li	0.269 8(6)	0.451 6(9)	0.826 3(12)			
N	0.203 6(3)	0.320 7(4)	0.764 4(5)	0.284 9(3)	0.639 8(4)	0.811 8(5)
C(1)	0.141 3(4)	0.308 1(6)	0.693 3(9)	0.350 5(4)	0.678 7(6)	0.857 9(8)
C(2)	0.148 3(6)	0.239 2(8)	0.568 5(10)	0.371 4(5)	0.802 5(7)	0.848 0(9)
C(3)	0.223 3(6)	0.182 2(7)	0.508 5(8)	0.324 0(4)	0.892 5(6)	0.787 5(8)
C(4)	0.286 9(5)	0.190 8(6)	0.577 9(7)	0.256 4(4)	0.856 5(5)	0.739 8(7)
C(5)	0.278 0(3)	0.257 8(5)	0.713 8(6)	0.237 3(3)	0.729 1(5)	0.752 9(6)
C(6)	0.339 4(3)	0.265 2(5)	0.801 9(6)	0.163 6(3)	0.687 0(5)	0.701 9(6)
Si(1)	0.302 3(1)	0.241 5(2)	1.007 3(2)	0.183 1(1)	0.684 5(2)	0.489 0(2)
C(11)	0.220 5(4)	0.125 6(6)	1.054 9(7)	0.278 2(5)	0.579 2(9)	0.434 7(9)
C(12)	0.258 2(5)	0.390 4(7)	1.108 0(7)	0.098 0(4)	0.610 0(7)	0.427 7(8)
C(13)	0.384 6(5)	0.178 5(10)	1.108 9(9)	0.200 9(7)	0.840 8(8)	0.393 3(9)
Si(2)	0.448 5(1)	0.260 3(2)	0.714 6(2)	0.064 4(1)	0.758 9(2)	0.810 8(2)
C(21)	0.504 4(4)	0.364 7(7)	0.816 8(8)	0.030 8(5)	0.912 8(7)	0.724 8(12)
C(22)	0.466 3(4)	0.325 9(7)	0.514 6(7)	−0.016 6(4)	0.644 0(7)	0.819 4(9)
C(23)	0.504 6(4)	0.099 4(7)	0.709 3(10)	0.076 4(5)	0.784 5(10)	1.005 5(9)

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

Atom	*x*	*y*	*z*
Li	0.051 3(5)	0.393 3(6)	0.481 5(5)
Ligand			
N	0.016 1(2)	0.352 0(3)	0.323 4(2)
C(1)	0.011 0(3)	0.239 7(4)	0.261 6(3)
C(2)	−0.022 6(3)	0.234 5(4)	0.149 0(3)
C(3)	−0.051 0(3)	0.353 8(5)	0.098 9(3)
C(4)	−0.045 6(3)	0.470 1(4)	0.159 1(3)
C(5)	−0.010 5(2)	0.471 1(3)	0.275 0(2)
C(6)	0.003 0(2)	0.593 3(3)	0.344 6(2)
Si(1)	0.142 07(7)	0.635 57(10)	0.360 84(8)
C(11)	0.168 4(3)	0.800 3(4)	0.432 9(4)
C(12)	0.221 1(3)	0.512 4(5)	0.449 2(4)
C(13)	0.203 3(3)	0.640 0(5)	0.221 3(3)
Si(2)	−0.084 81(8)	0.734 63(11)	0.302 37(8)
C(21)	−0.106 2(4)	0.845 2(4)	0.428 5(3)
C(22)	−0.041 5(4)	0.850 0(4)	0.188 6(3)
C(23)	−0.218 4(3)	0.677 3(5)	0.254 0(4)

Table 3. Non-hydrogen atom co-ordinates of compound (**3**)

Atom	*x*	*y*	*z*
Li	0.174 6(18)	0.276 5(11)	0.529 2(10)
Ligand			
N	0.138 4(7)	0.308 2(5)	0.639 3(4)
C(1)	0.072 4(10)	0.376 0(7)	0.672 0(6)
C(2)	0.128 0(11)	0.426 6(7)	0.737 3(6)
C(3)	0.262 9(11)	0.408 6(6)	0.770 3(6)
C(4)	0.333 4(10)	0.338 0(6)	0.739 7(6)
C(5)	0.272 1(9)	0.285 5(6)	0.673 5(5)
C(6)	0.337 6(8)	0.213 2(6)	0.638 7(5)
Si(1)	0.242 9(3)	0.108 6(2)	0.614 5(2)
C(11)	0.057 0(10)	0.109 3(7)	0.638 0(6)
C(12)	0.236 6(11)	0.075 1(7)	0.502 8(6)
C(13)	0.322 3(12)	0.011 2(7)	0.675 7(7)
Si(2)	0.531 1(3)	0.208 0(2)	0.652 1(2)
C(21)	0.618 0(10)	0.319 1(7)	0.642 2(7)
C(22)	0.614 9(11)	0.163 2(8)	0.753 9(7)
C(23)	0.596 4(11)	0.134 9(8)	0.572 3(7)
tmen			
N(01)	−0.005 0(8)	0.273 6(5)	0.435 6(5)
C(01)	0.032 8(13)	0.329 9(11)	0.377 1(8)
C(011)	−0.118 3(12)	0.312 2(10)	0.472 9(7)
C(012)	−0.060 5(15)	0.193 9(9)	0.393 5(9)
N(02)	0.252 1(8)	0.375 8(6)	0.462 1(5)
C(02)	0.130 5(12)	0.398 9(9)	0.401 7(8)
C(021)	0.297 7(12)	0.451 8(7)	0.514 2(8)
C(022)	0.370 3(13)	0.343 6(10)	0.421 3(8)

Structures based on 2-$Me_3SiCHC_5H_4N^-$. All three structures are different; (**4**) and (**5**) are dimeric with the anionic ligand bridging in different modes, and (**6**) is monomeric although with an η^3-aza-allyl type interaction as in (**4**). The Li–N,–C(6), and –C(5) distances in (**4**) and (**6**), and also the related compound, (**7**), are respectively, 2.19(1), 1.98(5), and 2.07$_2$; 2.36(1), 2.323(6), and 2.27$_0$; and 2.34(1), 2.353(6), and 2.25$_9$ Å, similar to those established in (**1**) and (**3**) above.

Complex (**4**) has an eight-membered ring with respect to the *ipso*-carbon and nitrogen centres, as in (**2**), but there are additional lithium-anion contacts, *viz*. Li–C(5), and the nitrogen now bridges two lithiums (Figure 4, and Figure 3 of ref. 12*b*). In addition, each lithium is bound by diethyl ether, above and below the η^3-aza-allyl planes; Li–O is 1.91(1) Å, similar to 1.94(3) Å in $[\{Li(OEt_2)[\mu\text{-}N(SiMe_3)_2]\}_2]$.[45] The Li–N distance common to both structures is 2.04(1) Å in (**4**), marginally longer than in (**2**), as a consequence of more electron density on the metal centres in (**4**). As in η^3-aza-allyl-containing structures for 2-$(Me_3Si)_2CC_5H_4N$, the N–C(5) and C(4)–C(5) distances are long, 1.395(7) and 1.43(1) Å, and the C(5)–C(6) distance short, 1.397(10) Å, compared with the analogous values for the neutral ligand in (**1**). The same applies to complex (**6**) [corresponding values 1.381(4), 1.426(4), and 1.400(4) Å], and for both (**4**) and (**6**) representation (**10**), with appropriate change of *ipso*-carbon atom substituents, is applicable. The Li ··· Li distance, 2.636(13) Å, is longer than in (**2**), and in the related complex (**8**), 2.544(2) Å.[13] There is a remarkable resemblance of the structure of (**4**) to that of (**8**), although this does not appear to have been recognized by the authors.[13]

Complex (**5**) is also binuclear, but in a different way, with a crystallographic C_2 axis passing through the tmen ligands and an Li_2N_2 core as part of the well known square arrangement for these two elements.[45] The anion now acts as an amido ligand, with C(5)–C(6) as an exocyclic double bond, distance 1.371(7) Å, and C–C bonds within the ring alternating in length with distances suggesting double- and single-bond character: C(1)–C(2) 1.35(1), C(2)–C(3) 1.42(1), and C(4)–C(5) 1.45(1) Å. Commensurate with this are rather long N–C(1), –C(5) distances [1.35(1), 1.39(1) Å]. As in (**4**) and (**6**), the Si is coplanar with the ring, deviation 0.06 Å, and is directed away from the

Table 4. Non-hydrogen atom co-ordinates of compound (**4**)

Atom	*x*	*y*	*z*
Li	0.077 4(8)	0.916 9(9)	0.403 1(10)
Ligand			
N	0.132 9(4)	0.979 3(4)	0.607 8(4)
C(1)	0.198 5(7)	1.063 8(6)	0.600 6(7)
C(2)	0.336 3(7)	1.010 8(8)	0.634 6(7)
C(3)	0.415 8(6)	0.857 7(9)	0.675 3(7)
C(4)	0.375 4(6)	0.770 1(7)	0.685 7(7)
C(5)	0.212 0(6)	0.826 5(6)	0.655 3(5)
C(6)	0.146 4(5)	0.737 5(6)	0.667 5(6)
Si(1)	0.217 4(2)	0.537 8(2)	0.723 2(2)
C(11)	0.070 3(8)	0.492 1(8)	0.742 4(10)
C(12)	0.328 0(8)	0.455 0(8)	0.560 9(10)
C(13)	0.322 9(7)	0.440 6(7)	0.927 7(8)
Ether			
0	0.192 7(4)	0.904 0(5)	0.214 0(5)
C(01)	0.206 1(8)	0.820 8(9)	0.103 2(9)
C(02)	0.099 5(8)	0.770 9(8)	0.130 1(9)
C(03)	0.321 8(11)	0.937 2(13)	0.206 2(13)
C(04)	0.269 6(14)	1.067 0(14)	0.115 7(15)

Table 5. Non-hydrogen atom co-ordinates of compound (**5**)

Atom	*x*	*y*	*z*
Li(A)	0.5(–)	0.367 6(11)	0.25(–)
Li(B)	0.5(–)	0.175 2(13)	0.25(–)
Ligand			
N	0.619 1(4)	0.280 3(4)	0.246 9(3)
C(1)	0.683 0(6)	0.292 2(6)	0.300 8(4)
C(2)	0.781 3(6)	0.288 6(6)	0.294 8(4)
C(3)	0.820 2(5)	0.272 5(6)	0.226 5(5)
C(4)	0.760 9(6)	0.258 8(6)	0.171 0(4)
C(5)	0.655 3(5)	0.262 3(6)	0.179 4(4)
C(6)	0.593 1(5)	0.247 3(5)	0.123 6(3)
Si(1)	0.625 7(2)	0.228 2(2)	0.030 5(1)
C(11)	0.703 2(7)	0.324 3(6)	−0.007 1(4)
C(12)	0.509 8(6)	0.225 2(6)	−0.023 6(4)
C(13)	0.695 1(7)	0.119 2(6)	0.015 3(5)
tmen (A)			
N(A1)	0.507 7(6)	0.479 4(5)	0.172 9(4)
C(A1)	0.479 4(8)	0.560 4(5)	0.212 3(5)
C(A11)	0.449 2(7)	0.474 3(6)	0.107 8(5)
C(A12)	0.612 1(6)	0.486 6(6)	0.152 0(4)
tmen (B)			
N(B1)	0.421 2(5)	0.064 7(5)	0.198 4(4)
C(B1)	0.480 4(7)	−0.016 0(5)	0.213 5(5)
C(B11)	0.403 3(7)	0.070 4(6)	0.122 0(5)
C(B12)	0.327 2(6)	0.056 9(5)	0.233 7(6)

nitrogen centre, most likely for steric reasons. Also the Si–C(6)–C(5) angle is enlarged relative to that expected for an *sp*^{2} carbon, possibly a consequence of release of steric strain associated with the silyl group. The Li $\cdots$ Li distance, 2.83(2) Å, is longer than in the other dimeric species; presumably the amido bridging mode is more adaptable to any repulsion between the metal centres. The bridging is unsymmetrical, Figure 5, although the Li–N(amido) distances, 2.077(9) and 2.25(1) Å, are within the limits found for other lithium amides;[45] associated N–Li–N angles for the two independent lithiums are 103.6(7) and 93.0(9)°.

The structure of compound (**6**) has already been discussed in comparisons above, except for the geometry for the Li(sp)$^+$ moiety [Li–N, 2.039 Å, N–Li–N, 91.5(2)°]. This differs marginally from that found in the only other structure of an organolithium–(−)sparteine complex, [$\{Li(CH_2PPhMe)(sp)\}_2$]-[Li–N, 2.10(2)—2.16(2) Å, N–Li–N 84.5(6) and 87.8(8)°].[11]

Table 6. Non-hydrogen atom co-ordinates of compound (**6**)

Atom	*x*	*y*	*z*
Li	1.014 7(3)	0.687 0(4)	0.211 1(5)
Aza-allyl ligand			
N	0.922 3(2)	0.604 1(2)	0.245 8(2)
C(1)	0.855 5(2)	0.601 4(2)	0.326 9(3)
C(2)	0.775 7(2)	0.599 8(3)	0.285 7(4)
C(3)	0.760 9(2)	0.603 6(3)	0.149 1(4)
C(4)	0.825 7(2)	0.606 1(2)	0.063 0(3)
C(5)	0.909 3(2)	0.603 7(2)	0.109 6(3)
C(6)	0.978 6(2)	0.604 0(2)	0.025 5(3)
Si	0.985 81(6)	0.611 25(8)	−0.153 74(9)
C(11)	0.932 0(3)	0.708 5(4)	−0.225 6(4)
C(12)	1.096 6(3)	0.625 4(4)	−0.199 6(4)
C(13)	0.945 6(5)	0.512 8(5)	−0.241 2(5)
Sparteine ligand			
N(A1)	1.139 1(2)	0.690 5(2)	0.257 7(2)
C(A2)	1.175 0(2)	0.607 2(2)	0.211 9(3)
C(A3)	1.261 0(2)	0.585 5(3)	0.264 2(4)
C(A4)	1.260 8(2)	0.588 4(3)	0.414 9(4)
C(A5)	1.229 0(3)	0.676 4(3)	0.462 8(4)
C(A6)	1.143 4(2)	0.697 5(2)	0.405 8(3)
C(A7)	1.111 4(3)	0.786 8(2)	0.451 0(3)
C(A8)	1.019 7(3)	0.802 5(2)	0.426 6(4)
N(B1)	0.998 0(2)	0.809 6(2)	0.283 4(3)
C(B2)	0.910 7(2)	0.838 3(3)	0.271 0(4)
C(B3)	0.883 7(2)	0.846 7(3)	0.129 2(5)
C(B4)	0.940 0(2)	0.906 0(3)	0.049 4(4)
C(B5)	1.029 2(2)	0.877 2(2)	0.067 9(4)
C(B6)	1.052 4(2)	0.873 2(2)	0.214 2(4)
C(B7)	1.143 8(2)	0.854 2(2)	0.239 9(4)
C(B8)	1.175 8(2)	0.766 9(2)	0.189 4(3)
C(AB)	1.159 9(3)	0.860 7(3)	0.389 0(4)

Complexes (**5**) and (**6**) have the same anion, and a bidentate tertiary amine, yet have different structures. Factors determining this difference may be electronic in nature, or steric since the amines have different normalized 'bites,' as judged by the difference in the angles subtended by the nitrogen centres of the tertiary amines, 83.2(6) and 83.7(7)[(**5**)] and 91.5(2)°[(**6**)]. It is also likely that crystal-packing forces may be important if the energy differences between the two structures are sufficiently small. In this context the isolation of polymorphs of organolithium–tmen complexes,[8c,46] differing only in the mode of interaction of the metal centres with the anions, is noteworthy.

In conclusion, it appears that both steric and electronic factors seem to interplay in determining the nature of the lithium–hydrocarbyl interactions, the electron-density distribution in the hydrocarbyl group, and also the degree of association for the system studied. The present study, and previous studies,[12,16–18] clearly establish that the ligands $2\text{-}Me_3SiCRC_5H_4N$ are capable of bonding in a variety of ways, readily adapting to the electronic and steric requirements of metal centres and associated ligands. With respect to organolithium chemistry, it is also established that the choice of solvent, and degree of substitution at the *ipso*-carbon, dramatically effects the nature of the product, as established for structures in the solid.

Experimental

Materials and Methods.—All the lithium compounds are extremely air and moisture sensitive and were handled under

Table 7. Lithium environments of compounds (**1**)—(**6**): *r* (Å) is the metal–ligand distance; other entries in the matrix are the angles (°) subtended at the lithium by the relevant atoms at the head of the row and column

Compound (**1**)

	r	N(B)	C(5)	C(6)
N(A)	2.00(1)	142.1(6)	36.2(2)	68.9(3)
N(B)	2.01(1)		150.6(5)	142.0(5)
C(5)	2.32(1)			36.6(3)
C(6)	2.22(1)			

Deviation of Li from C_5N plane of ligand A: 1.11 Å

Compound (**2**)

	r	C(6′)
N	1.936(6)	146.9(4)
C(6′)	2.213(7)	

Deviations of Li, Li′ from C_5N plane: −0.01, −1.21 Å, Li • • • Li′ 2.560(9) Å

Compound (**3**)

	r	C(5)	C(6)	N(01)	N(02)
N	1.96(2)	34.0(4)	64.8(5)	116.8(9)	116.2(9)
C(5)	2.46(2)		33.6(4)	150.0(9)	111.6(8)
C(6)	2.43(2)			154.5(9)	116.4(8)
N(01)	2.17(2)				86.4(7)
N(02)	2.06(2)				

Deviation of Li from C_5N plane: 1.11 Å

Compound (**4**)

	r	N	O	C(5)	C(6)
N	2.192(11)	103.0(4)	116.7(6)	35.6(2)	63.6(3)
N′	2.039(10)		126.3(4)	123.1(4)	106.4(4)
O	1.913(10)			110.0(5)	122.7(4)
C(5)	2.343(10)				34.6(3)
C(6)	2.356(9)				

Deviations of Li, Li′ from C_5N plane: 0.34, −1.70 Å, Li • • • Li′ 2.64(1) Å

Compound (**5**)

Li(A)	*r*	N′	N(A1)	N(A1)
N	2.08(1)	103.6(7)	114.0(3)	121.3(3)
N(A1)	2.20(1)			83.2(6)
Li(B)	*r*	N′	N(B1)	N(B1′)
N	2.25(1)	93.0(9)	149.3(3)	99.5(2)
N(B1)	2.18(2)			83.7(7)

Li(A) • • • Li(B) 2.83(2) Å

Compound (**6**)

	r	C(5)	C(6)	N(A1)	N(B1)
N	1.985(6)	35.9(1)	66.8(2)	135.1(3)	115.1(3)
C(5)	2.353(6)		34.8(1)	144.6(3)	123.8(2)
C(6)	2.323(6)			116.1(2)	139.3(3)
N(A1)	2.059(6)				91.5(2)
N(B1)	2.019(6)				

Deviation of Li from C_5 plane: 1.251 Å

an argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from sodium–benzophenone (diethyl ether), Na (benzene and toluene), $LiAlH_4$ [pentane and tetrahydrofuran(thf)], and CaH_2 (hexane) under a dinitrogen atmosphere prior to use.

Hydrogen-1 n.m.r. and mass spectra were recorded on Hitachi-Perkin-Elmer R-24B (60 MHz), Bruker WP-80 (80 MHz) and HX-90 (90 MHz), and Hewlett Packard-4986 spectrometers respectively. Carbon-13 (^1H decoupled) and lithium-6,7 n.mr. spectra were obtained on Bruker WP-80 and AM-300 spectrometers. Chemical shifts (δ) are reported relative to $SiMe_4$ (^1H, external), C_6D_6 or $CDCl_3$ (^{13}C), and aqueous $LiNO_3$ (^7Li, external). Elemental analyses were performed by the Canadian Microanalytical Laboratory and the Australian Mineral Development Laboratories. Optical rotations were obtained on a Perkin-Elmer 141 polarimeter at 20 °C using a cell (1 cm^3) with a path length of 1 dm (concentrations, *c* are quoted in mg cm^{-3}).

The compounds tmen and (−)sparteine sulphate were purchased from Aldrich and anhydrous (−)sparteine was prepared by treatment of the sulphate with NaOH, filtration, and distillation *in vacuo*; $LiBu^n$ and $MgBu^nBu^s$ were purchased from Metallgesellschaft and Alfa, respectively.

Preparations.—2-(*Trimethylsilylmethyl*)*pyridine*. To an ice-cooled solution of $LiBu^n$ (15.0 cm^3, 1.60 mol dm^{-3}, 24.0 mmol) and tmen (3.57 cm^3, 24.0 mmol), 2-methylpyridine (1.86 g, 20.0 mmol) was slowly added yielding an orange solid. After 1 h the solvent was removed *in vacuo* and the residue dissolved in diethyl ether (30 cm^3). This was then slowly added to a stirred solution of $SiMe_3Cl$ (3.0 cm^3, 24.0 mmol) in diethyl ether (30 cm^3) at 35 °C yielding a white precipitate. After 12 h at room temperature the solution was filtered, volatiles removed *in vacuo*, and the required compound distilled as a colourless *liquid*, b.p. 26 °C(0.1 mmHg), yield 2.7 g(82%). N.m.r. ($CDCl_3$): ^1H, δ −0.05 (s, 9 CH, $SiMe_3$), 2.10 (s, 2 H, CH), 6.8 (m, 2 H, C_5H_4N), 7.25 (m, 1 H, C_5H_4N), and 8.35 (m, 1 H, C_5H_4N); ^{13}C, δ −1.8 ($SiMe_3$), 30.0 (CH_2), 119.0, 121.9, 135.6, 148.9 (CH, C_5H_4N), and 161.3 p.p.m. (C, C_5H_4N).

2-[*Bis*(*trimethylsilyl*)*methyl*]*pyridine*. To an ice-cooled solution of $LiBu^n$ (20.0 cm^3, 1.6 mol dm^{-3}, 31.9 mmol) and tmen (4.72 cm^3, 31.9 mmol) was slowly added 2-methylpyridine (2.5 cm^3, 27.1 mmol) yielding an orange precipitate. The compound $SiMe_3Cl$ (3.43 cm^3, 27.1 mmol) was then added slowly over 30 min, yielding a pale yellow solution which over 12 h became colourless. The white precipitate was filtered off, volatiles removed *in vacuo*, and the required compound distilled as a colourless *liquid*, b.p. 47 °C (0.1 mmHg), yield 2.7 g (85%). N.m.r. ($CDCl_3$): ^1H, δ −0.07 (s, 18 H, $SiMe_3$), 2.20 (s, 1 H, SiCH), 6.70 (m, 2 H, C_5H_4N), 7.38 (m, 1 H, C_5H_4N), and 8.25 (m, 1 H, C_5H_4N); ^{13}C, δ 0.0 ($SiMe_3$), 33.4 (SiCH), 118.0, 122.8, 135.5, 149.2 (CH, C_5H_4N), and 164.4 p.p.m. (C, C_5H_4N).

2-[*Tris*(*trimethylsilyl*)*methyl*]*pyridine*. A solution of $LiBu^n$ (0.7 cm^3, 1.6 mol dm^{-3}, 1.12 mmol) and tmen (0.17 cm^3, 1.12 mmol) was cooled to 0 °C and 2-[bis(trimethylsilyl)methyl]pyridine (0.23 g, 0.95 mmol) slowly added yielding a deep red solution. The compound $SiMe_3Cl$ (0.15 g, 1.4 mmol) was then added and after 30 min the solution was filtered, washed with water (2 × 5 cm^3), and concentrated *in vacuo*. The resulting solid residue was crystallized from ethanol yielding colourless *needles* of the required compound, m.p. 204 °C, yield 0.48 g (75%). N.m.r: ^{1}H ($CDCl_3$), δ 0.10 (s, 27 H, $SiMe_3$), 7.00 (m, 3 H, C_5H_4N), and 8.20 (m, 1 H, C_5H_4N); ^{13}C (C_6D_6), 4.2 ($SiMe_3$), 118.7, 124.7, 135.0, 147.7 (CH, C_5H_4N), and 164.9 p.p.m. (C, C_5H_4N).

$[Li\{2\text{-}C(SiMe_3)_2C_5H_4N\}\{2\text{-}CH(SiMe_3)_2C_5H_4N\}]$ **(1)**. 2-[Bis(trimethylsilyl)methyl]pyridine (0.3 g, 1.23 mmol) was added to $LiBu^n$ (0.80 cm^3, 1.6 mol dm^{-3}, 1.28 mmol) yielding a red solution which on standing at room temperature for 12 h gave yellow *prisms* of the required complex. These were isolated, washed with pentane (3 × 5 cm^3) and dried *in vacuo*, m.p. 106—108 °C, yield 0.20 g (67%). N.m.r. (C_6D_6, prime denotes anionic ligand): ^{1}H, δ 0.00 (s, 18 H, $SiMe_3$), 0.50 (s, 18 H, $SiMe_3$), 1.95 (s, 1 H, SiCH), 6.32 (m, 2 H, C_5H_4N), 6.50 (m, 2 H, C_5H_4N), 6.92 (m, 1 H, C_5H_4N), 7.15 (m, 1 H, C_5H_4N'), and 8.21 (m, 1 H, C_5H_4N'); ^{13}C, δ −0.2 ($SiMe_3$), 34.5 (SiCH), 119.5, 123.2, 137.2, 148.9 (CH, C_5H_4N), 164.2 (C, C_5H_4N); 4.28 ($SiMe_3'$), 122.1 (CLi), 110.6, 124.7, 134.7, 147.4 (CH, C_5H_4N'), and 176.6 p.p.m. (C, C_5H_4N'); ^{7}Li, δ 0.06 p.p.m.

$[\{Li[2\text{-}C(SiMe_3)_2C_5H_4N]\}_2]$ **(2)**. To a solution of $LiBu^n$ (0.72 cm^{-3}, 1.6 mol dm^{-3}, 1.22 mmol) was slowly added diethyl ether (0.5 cm^3) then 2-[bis(trimethylsilyl)methyl]pyridine (0.3 g, 1.2 mmol) with minimal stirring. During 8 h at room temperature pale yellow *prisms* of the required complex crystallized. These were collected, washed with pentane (3 × 5 cm^2), and dried *in vacuo*, m.p. 132—134 °C, yield 0.22 g (72%). N.m.r. (C_6D_6): ^{1}H, δ 0.28 (s, 18 H, $SiMe_3$), 6.27 (m, 1 H, C_5H_4N), 6.92 (m, 2 H, C_5H_4N), and 7.78 (m, 1 H, C_5H_4N): ^{13}C, δ 3.5 ($SiMe_3$), 105.3 (CLi), 112.7, 125.8, 135.7, 146.8 (CH, C_5H_4N), and 175.9 p.p.m. (C, C_5H_4N); ^{7}Li, δ 1.24 p.p.m.

$[Li(tmen)\{2\text{-}C(SiMe_3)_2C_5H_4N\}]$ **(3)**. A solution of $LiBu^n$ (0.7 cm^3, 1.6 mol dm^{-3}, 1.12 mmol) and tmen (0.17 cm^3, 1.12 mmol) was cooled to 0 °C and 2-bis[(trimethylsilyl)methyl]-pyridine (0.23 g, 0.95 mmol) slowly added yielding a deep red solution. During 12 h at room temperature orange *crystals* of the required complex formed. These were collected, washed with pentane (3 × 5 cm^3), and dried *in vacuo*, m.p. 83—85 °C, yield 0.32 g (92%). ^{1}H N.m.r. (C_6D_6): ^{1}H, δ 0.45 (s, 18 H, $SiMe_3$), 1.85 (s, 12 H, CH_3), 1.95 (s, 4 H, CH_2), 6.25 (m, 2 H, C_5H_4N), 7.08 (m, 1 H, C_5H_4N), and 7.75 (m, 1 H, C_5H_4N); ^{13}C, δ 4.8 ($SiMe_3$), 45.5 (NCH_3), 56.8 (NCH_2), 108.9 (LiCSi), 118.4, 124.0, 133.9, 146.9 (CH, C_5H_4N), and 175.0 p.p.m. (C, C_5H_4N); ^{7}Li, δ −0.68 p.p.m.

$[\{Li(OEt_2)[2\text{-}CH(SiMe_3)C_5H_4N]\}_2]$ **(4)**. To a stirred solution of $LiBu^n$ in diethyl ether (1.00 cm^3, 1.6 mol dm^{-3}, 1.7 mmol) was slowly added 2-(trimethylsilylmethyl)pyridine (0.31 g, 1.31 mmol) yielding an orange solution. During *ca.* 12 h at room temperature pale yellow *prisms* of the required complex formed. These were collected, washed with pentane (3 × 5 cm^3), and dried *in vacuo*, m.p. 88—90 °C, yield 0.24 g (74%). N.m.r. (C_6D_6): ^{1}H, δ 0.51 (s, 9 H, $SiMe_3$), 1.2 (t, 6 H, CCH_3), 2.9 (s, 1 H, SiCH), 3.3 (q, 4 H, OCH_2), 5.9 (m, 1 H, C_5H_4N), 6.7 (m, 2 H, C_5H_4N), and 7.8 (m, 1 H, C_5H_4N); ^{13}C, δ 1.4 ($SiMe_3$), 14.8 ($C\mathit{C}H_3$), 60.9 (OCH_2), 65.7 (SiCH), 103.2, 117.5, 134.3, 148.2 (CH, C_5H_4N), and 166.9 p.p.m. (C, C_5H_4N); ^{7}Li, δ 0.83 p.p.m.

$[\{Li(tmen)[2\text{-}CH(SiMe_3)C_5H_4N]\}_2]$ **(5)**. To a solution of $LiBu^n$ (0.7 cm^3, 1.6 mol dm^{-3}, 1.12 mmol) and tmen (0.17 cm^{-3}, 1.12 mmol) at 0 °C 2-(trimethylsilylmethyl)pyridine (0.17 g, 1.0 mmol) was slowly added yielding a deep red solution. During *ca.* 12 h, at room temperature orange *crystals* of the required complex deposited. These were washed with pentane (3 × 5 cm^3) and dried *in vacuo*, m.p. 106—108 °C, yield 0.29 g (92%). N.m.r. (C_6D_6): ^{1}H, δ 0.4 (s, 9 H, $SiMe_3$), 1.1 (s, 4 H, NCH_2), 1.2 (s, 12 H, NCH_3), 3.1 (s, 1 H, SiCH), 5.3 (m, 1 H, C_5H_4N), 6.5 (m, 2 H, C_5H_4N), and 7.2 (m, 1 H, C_5H_4N): ^{13}C, δ 1.5 ($SiMe_3$), 46.8 (NCH_3), 57.9 (NCH_2), 65.7 (SiCH), 100.6, 117.5, 134.3, 148.2 (CH, C_5H_4N), and 168.7 p.p.m. (C, C_5H_4N); ^{7}Li, δ −0.92 p.p.m.

$[Li\{2\text{-}CH(SiMe_3)C_5H_4N\}_2\{2\text{-}CH_2(SiMe_3)C_5H_4N\}]$. 2-(Trimethylsilylmethyl)pyridine (0.5 g, 3.2 mmol) was added to $LiBu^n$ (1.38 cm^3, 1.6 mol dm^{-3}, 2.2 mmol) yielding an orange solution. During *ca.* 12 h at room temperature yellow *crystals* of the required complex formed. These were isolated, washed with pentane (3 × 5 cm^3), and dried *in vacuo*, m.p. 106—108 °C yield 0.34 g (67%). N.m.r. (C_6D_6): ^{1}H, δ 0.0 (s, 9 H, $SiMe_3$), 2.22 (s, 2 H, CH_2), 6.82 (m, 2 H, C_5H_4N), 7.23 (m, 1 H, C_5H_4N), and 8.15 (m, 1 H, C_5H_4N); 0.04 (s, 18 H, $SiMe_3'$), 2.80 (s, 2 H, SiCH′), 5.74 (m, 4 H, C_5H_4N'), 6.87 (m, 2 H, C_5H_4N'), and 8.06 (m, 2 H, C_5H_4N'); ^{13}C, δ −1.8 ($SiMe_3$), 29.9 (CH_2), 119.7, 123.0, 134.8, 149.3 (CH, C_5H_4N), and 162.1 (C, C_5H_4N); 1.4 ($SiMe_3'$), 59.9 (SiCH′), 104.3, 117.9, 137.1, 148.5 (CH, C_5H_4N'), and 167.9 p.p.m. (C, C_5H_4N'); ^{7}Li, δ 0.00 p.p.m.

$[Li(sp)\{2\text{-}CH(SiMe_3)C_5H_4N\}]$ **(6)**. 2-(Trimethylsilylmethyl)pyridine (0.5 g, 3.0 mmol) was added to a solution of $LiBu^n$ (2.3 cm^3, 1.6 mol dm^{-3}, 3.6 mmol) and sp (0.8 cm^3, 3.6 mmol) in diethyl ether (20 cm^3) at room temperature. After 12 h the resulting orange crystalline *solid* of the required complex was collected, washed with cold pentane (3 × 5 cm^3), and dried *in vacuo*, m.p. 56 °C (decomp.), yield 1.1 g (94%). N.m.r. (C_6D_6): ^{1}H, δ 0.44 (s, 9 H, $SiMe_3$), 1.03—3.10 (m, 27 H, sp, CH), 5.79 (m, 1 H, C_5H_4N), 6.68 (m, 2 H, C_5H_4N), and 7.56 (m, 1 H, C_5H_4N); ^{13}C, δ 1.8 ($SiMe_3$), 60.5 (SiCH), 102.3, 115.5, 133.8, 148.6 (CH, C_5H_4N), 168.2 (C, C_5H_4N); 18.1 (C^{15}), 24.2, 24.6, 24.8, 25.1 ($C^{2,3,9,10}$), 28.2, 30.0 ($C^{1,8}$), 35.1 ($C^{7,14}$), 45.7, 52.5, 57.6, 61.5 ($C^{4,6,11,13}$), 56.1, and 66.7 p.p.m. ($C^{7a,14a}$, and all sp); ^{7}Li, δ −0.56 p.p.m.

2-[(1′-*Trimethylsilyl*)*ethyl*]*pyridine*. *Method* (*a*). Methyl iodide (2.3 cm^3, 37.5 mmol) was added to a solution of compound **(6)** (4.75 g, 11.7 mmol) in hexane (20 cm^3) at −78 °C. After 1 h the mixture was warmed to room temperature and stirred for 4 h. The required compound was extracted into hexane and distilled, b.p. 28 °C (0.1 mmHg), yield 1.4 g (64%). N.m.r. ($CDCl_3$): ^{1}H, δ −0.35 (s, 9 H, $SiMe_3$), 1.06 (d, 3 H, CCH_3, $J = 7$), 2.05 (q, 1 H, MeCH, $J = 7$ Hz), 6.5 (m, 2 H, C_5H_4N), 7.0 (m, 1 H, C_5H_4N), and 8.1 (m, 1 H, C_5H_4N); ^{13}C, δ −3.6 ($SiMe_3$), 13.4 ($C\mathit{C}H_3$), 32.3 ($Me\mathit{C}H$), 118.9, 120.8, 135.1, 148.4 (CH, C_5H_4N), and 165.4 p.p.m. (C, C_5H_4N) (Found: C, 66.85, H, 9.40; N, 8.00. Calc. for $C_{10}H_{17}NSi$: C, 66.95; H 9.55; N, 7.80%); m/z 179 (P^+); α (589 nm) −1.3, α (436 nm) = −6.1, α (365 nm) = −17.9° ($c = 81$, Et_2O).

Method (*b*). 2-(Trimethylsilylmethyl)pyridine (0.5 g, 3.0 mmol) was slowly added to a stirred solution of $MgBu^nBu^s$ (4.4 cm^3, 0.70 mol dm^{-3}, 3.1 mmol) and sp (0.7 cm^3, 3.1 mmol) in diethyl ether (10 cm^3) and stirred for 12 h. The solvent was then removed *in vacuo*, hexane (10 cm^3) added, and the solution cooled to −95 °C, whereupon MeI (1 cm^3, 16.0 mmol) was slowly added with stirring. The required compound was extracted and distilled as above, yield 0.2 g (35%), α (589 nm) = −0.4, α (436 nm) = −2.0° ($c = 69$, Et_2O).

3-(*Trimethylsilylmethyl*)*pyridine*. Hexamethylphosphoramide (11.4 cm^3, 65.1 mmol) was added slowly to a solution of $LiNPr^i_2$ (54.0 cm_3, 1.26 mol dm^{-3} in hexane, 68.0 mmol) (prepared from $LiBu^n$ and $NHPr^i_2$) at 0 °C and stirred for 30 min. 3-Methylpyridine (6.0 cm^3, 61.6 mmol) in thf (20 cm^3) was then added with stirring and the resulting red solution stirred for 30 min. The compound $SiMe_3Cl$ (10.0 cm^3, 78.8 mmol) in thf (20 cm^3) was slowly added and the mixture stirred for 1 h at room temperature. The solvent was removed *in vacuo*, and the required compound extracted into hexane and distilled, yield 5.6 g (55%), b.p. 38 °C (1.0 mmHg). N.m.r. (C_6D_6): ^{1}H, δ −0.16 (s, 9 H, $SiMe_3$), 17.4 (s, 2 H, $SiCH_2$), 6.85 (m, 2 H, SiC_5H_4N), and 7.35 (m, 2 H, C_5H_4N); ^{13}C, δ −2.3 ($SiMe_3$), 23.6 (CH_2), 123.0, 134.7, 146.1, 149.8 (CH, C_5H_4N), and 135.9 p.p.m. (C, C_5H_4N) (Found: C, 65.85; H, 9.25; N, 8.90. Calc. for $C_9H_{15}NSi$: C, 65.40; H, 9.15, N, 8.45%); m/z 165 (P^+).

$[Li(tmen)\{3\text{-}CH(SiMe_3)C_5H_4N\}]$. 3-(Trimethylsilylmethyl)pyridine (2.0 cm^3, 11.1 mmol) was added to a solution of LiBu^n (8.3 cm^3, 13.3 mmol) and tmen (20 cm^3, 13.3 mmol) and the mixture stored at −30 °C for 72 h. The resultant orange *solid* of the required compound was collected, washed with pentane (3 × 2 cm^3), and dried *in vacuo*, m.p. 62 °C (decomp.), yield 1.0 g (31%). N.m.r. (C_6D_6): ^{1}H, δ 0.4 (s, 9 H, $SiMe_3$), 2.01 (s, 16 H, CH_3N, CH_2N), 2.42 (s, 1 H, SiCH), 6.95 (m, 3 H, C_5H_4N), and 8.32 (s, 1 H, C_5H_4N); ^{13}C, δ 2.3 ($SiMe_3$), 4.60 (NCH_3), 57.4 (NCH_2), 69.7 (SiCH), 123.5, 123.8, 129.0, 129.9 (CH, C_5H_4N), and 154.2 p.p.m. (C, C_5H_4N); ^{7}Li, δ 0.83 p.p.m.

3-[*Bis*(*trimethylsilyl*)*methyl*]*pyridine*. To a stirred hexane (20 cm^3) solution of compound **(7)** (1.0 g, 3.5 mmol) at 0 °C, $SiMe_3Cl$ (1.0 cm^3, 7.9 mmol) was slowly added and the resulting solution stirred for 4 h. Volatiles were then removed *in vacuo* and the residue taken up in hexane. This was filtered, concentrated *in vacuo*, and the required compound distilled, b.p. 64 °C (0.1 mmHg), yield 0.1 g (15%). N.mr. (C_6D_6): ^{1}H, δ −0.05 (s, 18 H, $SiMe_3$), 1.29 (s, 1 H, CH), 6.85 (m, 2 H, C_5H_4N), and 8.35 (m, 2 H, C_5H_4N); ^{13}C, δ 0.0 ($SiMe_3$), 26.2 (SiCH), 122.9, 134.9, 145.6, 150.6 (CH, C_5H_4N), and 138.8 p.p.m. (C, C_5H_4N). *m*/*z* 237 (P^+).

4-(*Trimethylsilylmethyl*)*pyridine*. To a stirred thf (20 cm^3) solution of 4-methylpyridine (3.0 cm^3, 30.78 mmol) at −78 °C, $LiNPr^i_2$ (27 cm^3, 1.26 mol dm^{-3} in hexane, 34.0 mmol) was slowly added and the solution stirred for 1 h. The compound $SiMe_3Cl$ (5.0 cm^3, 39.3 mmol) was then added and the solution warmed to room temperature, stirred for 4 h, volatiles removed *in vacuo*, and the residue extracted with hexane. This was filtered and the required compound distilled, b.p. 42 °C (0.1 mmHg), yield 4.1 g (61%). N.m.r. (C_6D_6): ^{1}H, δ −0.16 (s, 9 H, $SiMe_3$), 1.79 (s, 2 H, CH_2), 6.65 (m, 2 H, C_5H_4N), and 8.38 (m, 2 H, C_5H_4N); ^{13}C, δ −2.2 ($SiMe_3$), 26.9 (CH_2), 123.6, 149.9 (CH, C_5H_4N), and 149.5 p.p.m. (C, C_5H_4N). *m*/*z* 165 (P^+).

[Li(tmen){4-CH($SiMe_3$)C_5H_4N}]. 4-(Trimethylsilylmethyl)pyridine (4.0 cm^3, 23.0 mmol) was added to a solution of LiBu^n (15.8 cm^3, 25.3 mmol) and tmen (3.8 cm^3, 25.3 mmol) at 0 °C. After 1 h the solvent was removed *in vacuo* and the yellow solid washed with pentane (3 × 5 cm^3) and dried *in vacuo*, m.p. 102 °C (decomp.), yield 3.4 g (89%). N.m.r. ([$^2H_8$]thf): ^{1}H, δ − 0.10 (s, 9 H, $SiMe_3$), 2.16 (s, 12 H, NCH_3), 2.32 (s, 4 H, NCH_2), 2.63 (s, 1 H, SiCH), 5.6 (m, 2 H, C_5H_4N), and 6.5 (m, 2 H, C_5H_4N); ^{13}C, δ 1.7 ($SiMe_3$), 46.4 (NCH_3), 58.4 (NCH_2), 70.2 (SiCH), 111.3, 116.0, 144.1, 144.5 (CH, C_5H_4N), and 156.3 p.p.m. (C, C_5H_4N); ^{7}Li, δ 0.40, (C_6D_6) −0.06 p.p.m.

[Li(sp){4-CH($SiMe_3$)C_5H_4N}]. 4-(Trimethylsilylmethyl)pyridine (0.4 cm^3, 3.0 mmol) was added to a solution of LiBu^n (2.3 cm^3, 3.7 mmol) and sp (0.8 cm^3, 3.6 mmol) in diethyl ether (5 cm^3) at room temperature. After 12 h the solvent was removed *in vacuo* and the yellow oil washed with cold pentane (4 × 3 cm^3), yielding a yellow *solid* of the required compound, m.p. 94.95 °C (decomp.), yield 0.7 g (60%). N.m.r. (C_6D_6): ^{1}H, δ 0.44 (s, 9 H, $SiMe_3$), 0.65—3.26 (m, 28 H, sp, CH_2), 6.35 (m, 2 H, C_5H_4N), and 7.2 (m, 2 H, C_5H_4N); ^{13}C, δ 1.8 ($SiMe_3$), 29.2 (SiCH), 112.5, 115.5, 145.2, 145.6 (CH, C_5H_4N), and 156.3 (C, C_5H_4N); 23.0 (C^{15}), 24.5(×2), 25.1, 25.5 ($C^{2,3,9,10}$), 28.1, 30.3 ($C^{1,8}$), 34.94 ($C^{7,14}$), 47.5, 53.6, 57.3, 61.4 ($C^{4,6,11,13}$), and 66.94 p.p.m. ($C^{7a,14a}$, all sp); ^{7}Li, δ 0.76 p.p.m.

4-[(1′-*Trimethylsilyl*)*ethyl*]*pyridine*. Methyl iodide (1.0 cm^3, 16.1 mmol) was added to a stirred hexane (20 cm^3) solution of compound **(9)** (2.0 g, 7.1 mmol) at −78 °C and the solution slowly warmed to room temperature over 18 h. Solvent was removed *in vacuo* and the required compound extracted into hexane and distilled, b.p. 48—50 °C (0.1 mmHg), yield 0.7 g (58%). N.m.r. (C_6D_6): ^{1}H, δ −0.19 (s, 9 H, $SiMe_3$), 1.11 (d, 3 H, CMe, J = 7 Hz), 1.84 (q, 1 H, SiCH, J = 7 Hz), 6.65 (m, 2 H, C_5H_4N), and 8.45 (m, 2 H, C_5H_4N); ^{13}C, δ −3.6 ($SiMe_3$), 29.8 (SiCH), 122.5 (CH, C_5H_4N), 149.9 (CH, C_5H_4N), and 154.6 p.p.m. (C, C_5H_4N) (Found: C, 67.45; H, 9.70; N, 7.75. Calc. for $C_{10}H_{17}NSi$: C, 66.95; H, 9.55; N, 7.75%); *m*/*z* 179 (P^+); α (589 nm) −0.2, α (435 nm) = −0.5 ° (c = 64, Et_2O).

Crystallography.—Specimens were enclosed in capillaries under argon for the *X*-ray work. Unique data sets were measured to the $2\theta_{max.}$ limit of the data using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers fitted with monochromatic Mo-K_α radiation sources and operating in conventional 2θ—θ scan mode. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement without absorption correction after solution of the structures by direct methods. Unless stated otherwise, anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included at idealized values. Residuals at convergence on $|F|$ are quoted, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral complex scattering factors were used;[47] computation used the XTAL 83[48] program system implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Non-hydrogen atom numbering is shown in the Figures.

Crystal data. **(1)**, $C_{24}H_{45}LiN_2Si_4$, M = 480.9, triclinic, space group $P\bar{1}$ (C^1_i, no. 2), 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 = 1 556(1) Å^3, D_c = 1.03 g cm^{-3} (Z = 2), F(000) = 524, μ_{Mo} = 2.0 cm^{-1}, specimen 0.38 × 0.34 × 0.40 mm, $2\theta_{max.}$ = 40 °, N = 3 824, N_o = 3 076, R = 0.053, R' = 0.058.

(2), $C_{24}H_{44}Li_2N_2Si_4$, M = 486.8, monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14), a = 12.905(6), b = 9.983(5), c = 11.799(5) Å, β = 93.56(4)°, U = 1 517(1) Å^3, D_c(Z = 2) = 1.07 g cm^{-3}, F(000) = 528, μ_{Mo} = 2.1 cm^{-1}, $2\theta_{max.}$ = 50°, N = 2 688, N_o = 2 045, R = 0.053, R' 0.056. Specimen: cuboid ≈0.4 mm.

(3) $C_{18}H_{38}LiN_3Si_2$, M = 359.6, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 9.606(4), b = 15.036(7), c = 16.60(1) Å, β = 97.40(3)°, U = 2 378(2) Å^3, D_c = 1.00 g cm^{-3} (Z = 4), F(000) = 792, μ_{Mo} = 1.5 cm^{-1}, specimen 0.5 × 0.4 × 0.45 mm, $2\theta_{max.}$ = 45°, N = 3 125, N_o = 1 515, R = 0.066, R' = 0.085.

(4) $C_{26}H_{48}Li_2N_2O_2Si_2$, M = 490.8, triclinic, space group $P\bar{1}$ (C^1_i, no. 2), 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 = 1), F(000) = 268, μ_{Mo} = 1.3 cm^{-1}, specimen 0.50 × 0.45 × 0.30 mm, $2\theta_{max.}$ = 45°, N = 2 093, N_o = 1 071; R = 0.056, R' 0.062.

(5) $C_{30}H_{60}Li_2N_6Si_2$, M = 575.0, orthorhombic, space group $Pbcn$ (D^{14}_{2h}, no. 60), a = 13.684(7), b = 14.699(9), c = 18.875(10) Å, U = 3 796(4) Å^3, D_c = 1.01 (Z = 4 dimers) g cm^{-3}, F(000) = 264, μ_{Mo} = 1.2 cm^{-1}, specimen 0.35 × 0.28 × 0.18 mm, $2\theta_{max.}$ = 45°, N = 2 399, N_o = 917, R = 0.074, R' = 0.020.

(6) $C_{24}H_{40}LiN_3Si$, M = 405.6, orthorhombic, space group $P2_12_12_1$ (D^4_2, no. 19), a = 16.125(3), b = 15.219(6), c = 10.018(2) Å, U = 2 458(1) Å^3, D_c = 1.10 (Z = 4), F(000) = 888, μ = 1.1 cm^{-1}, specimen 0.30 × 0.40 × 0.40 mm, $2\theta_{max.}$ = 55°, N = 3 998, N_o = 2 099, R = 0.049, R' = 0.051.

Abnormal features/*variations in procedure*. For compound **(1)**, (x, y, z, U_{iso}) were refined for the non-methyl hydrogen atoms; for **(2)**, $(x, y, z)_H$ were refined for the non-methyl hydrogen atoms, and for **(3)**, $(x, y, z)_H$ were refined for the non-methyl hydrogen atoms. Linewidths for this compound were wide and the precision of the cell calibration poor.

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

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