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Negative hyperconjugation control of acidities in α-trimethylsilyl substituted α-picolines: isolation of $[Li\{NC_5H_4\text{-}2\text{-}C(H)(SiMe_3)_2\}\{NC_5H_4\text{-}2\text{-}C(H)(SiMe_3)\}]_2$

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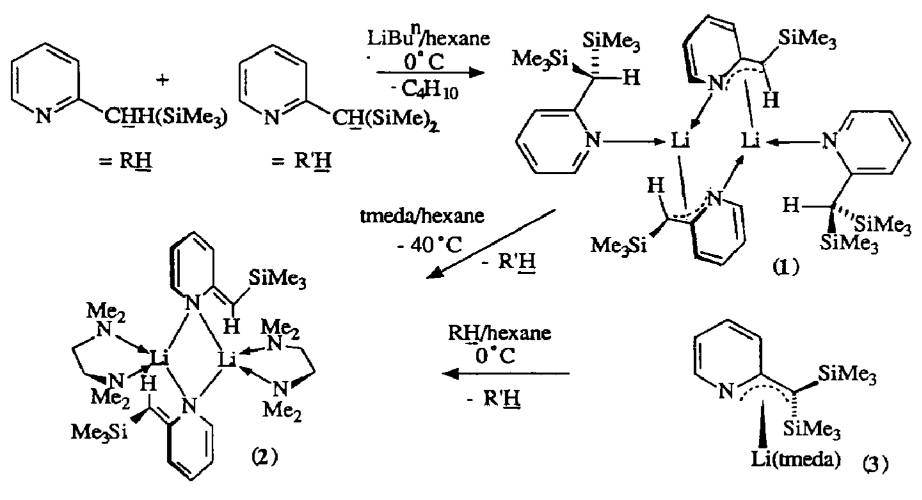
Abstract

Isolation of $[\{Li(R'H)(R)\}_2]$ (1) ($R^- = NC_5H_4\text{-}2\text{-}CH(SiMe_3)$, $R'H = NC_5H_4\text{-}2\text{-}CH(SiMe_3)_2$), where $R'H$ acts as an N-donor and R^- as an η^3-aza-allyl unit to one metal centre and an N-bridge to the other (X-ray structure determination), and formation of $[\{Li(R)(tmeda)\}_2]$ and $R'H$ on treatment of (1) with tmeda (= *N,N,N′,N′*-tetramethylethylenediamine) establishes the relative solution thermodynamic acidities $RH > R'H$, rationalized by negative hyperconjugation in RH overriding extra polarization from two silicon centres in $R'H$.

Silicon increases thermodynamic acidities of adjacent CH_n groups [1] facilitating metallation using strong bases such as alkyllithium reagents, and stabilizes the resulting anionic centre by the high polarizability of silicon [2]. As part of a systematic study of the lithiation of α-trimethylsilyl substituted α-picolines we show that incorporating two trimethylsilyl groups, $C_5H_4\text{-}2\text{-}CH(SiMe_3)_2$ (= $R'H$), results in a lower thermodynamic acidity relative to the compound with one such group, $NC_5H_4\text{-}2\text{-}CHH(SiMe_3)$ (= RH). Features of the research include the isolation and structure determination of a compound containing unmetallated $R'H$, yet metallated RH, $[\{Li(R'H)(R)\}_2]$ (1), and selected exchange reactions. Overall, the results explain why treatment of $Li(tmeda)(NC_5H_4CH_2\text{-}2)$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) with $ClSiMe_3$ yields RH, and α-picoline and $R'H$ (via quenching of the metallation product of preformed RH by $Li(tmeda)(NC_5H_4CH_2\text{-}2)$), but not $NC_5H_4C(SiMe_3)_3$[3], and also the lithiation of the monosilyl substituted carbon in $m\text{-}C_6H_4(CH_2SiMe_3)\{CH(SiMe_3)_2\}$ [4].

Synthesis of **1** and other reactions are summarized in Scheme 1 *. Treating a 1 : 1 mixture of RH and $R'H$ with one equivalent of $LiBu^n$ in hexane yields **1** in which $R'H$ simply acts as an N-donor. It is resistant to metallation in the presence of



excess LiBu^n and is therefore non-labile. Treating **1** with tmeda results in displacement of R'*H*, yielding the binuclear complex [{Li(R)(tmeda)}$_2$] (**2**)[3], which together with the formation of the same compound, **2**, on treating the bis-silylated analogue, [Li(R')(tmeda)] [3], with R*H* unequivocally shows that R*H* is a stronger acid than R'*H*, viz compound **1** is the thermodynamically controlled product.

Results of the X-ray structure determination of **1** * are presented in Fig. 1. Each anion acts as an η^3-aza-allyl unit to one lithium through the ring nitrogen, 2.14(1) Å, *ipso*-carbon, 2.39(1) Å, and adjacent ring carbon, 2.39(1) Å, with the nitrogen bridging the other metal centre, 2.06(1) Å, in a similar way to that found in [{Li(R)(OEt$_2$)}$_2$], corresponding distances 2.19(1), 2.356(9), 2.34(1), 2.04(1) Å [3], and in some related structures [5,6]. The silicon of R$^-$ is coplanar with the pyridine

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* *Synthesis and characterization of compound* (**1**): A solution of LiBu^n in hexane (4.2 ml, 1.55 *M*, 6.51 mmol) and hexane (20 ml) was slowly added to a solution of RH (1.05 g, 6.36 mmol) and R'H (1.5 g, 6.36 mmol) in hexane (40 ml) at 0 °C yielding a yellow solution. Volatiles were removed under vacuum to yield a yellow powder which was recrystallised from benzene (15 ml) affording orange crystals of **1** overnight at 5 °C (2.15 g, 83% yield). M.p. 145–147 °C (dec.); ^{1}H NMR (250 MHz, C_6D_6), δ (rel. TMS) 0.08 (18H, s, $SiCH_3$, R'*H*) 0.27 (9H, s, $SiCH_3$, R*H*) 2.11 (1H, broad s, CHSi, R'*H*) 3.20 (1H, s, CHSi, R*H*) 5.72 (1H, m, C_4H, R*H*) 6.4–7.0 (4H, m, $C_{3,5}$, R*H* and R'*H*) 7.78 (1H, m, C_6H, R*H*) 8.19 (1H, m, C_6H, R'*H*); ^{13}C NMR (62.8 MHz, C_6D_6), δ 0.2 (s, $SiCH_3$, R'*H*) 1.2 (s, $SiCH_3$, R*H*) 3.16 (s, CHSi, R'*H*) 63.3 (s, CHSi, R*H*) 103.0, 118.0, 119.0, 122.8, 134.2, 136.5, 149.1, 149.9, 165.0, 166.6. (NC_5H_4, R*H*, R'*H*); ^{7}Li NMR (116.64 MHz, C_6D_6) δ −1.67 (s). Anal. Found: C, 60.8; H, 9.05; N, 6.75%. $C_{42}H_{74}Li_2N_4Si_6$ requires C, 61.7; H, 9.13; N, 6.85%.

Crystal structure determination of **1** ($T = 296$ K; Enraf-Nonius CAD4 diffractometer, crystal mounted in a capillary): $C_{42}H_{82}Li_2N_4Si_6$, $M = 817.5$, monoclinic, space group $P2_1/n$, a 10.446(4), b 16.872(1), c 16.047(6) Å, β 108.32(2)°, U 2685(1) Å^3, F(000) = 888, Z = 2, D_c 1.01 g cm^{-3}, μ(Mo-K_α) = 1.83 cm^{-1}, specimen 0.75×0.35×0.35 mm, 3744 unique reflections, 2087 with $I > 2.5\sigma(I)$ used in the refinement, $2\theta_{max} = 50°$.

The structure was solved by direct methods and refined by full-matrix least-squares refinement with non-hydrogen atoms anisotropic. Hydrogen atoms were included as invariants with $U_{iso} = 0.05$ Å^2. The weighting scheme was $\omega = 1.9/[\sigma^2(F_o) + 1.5\times10^{-3}(F_o)^2]$ and the final residuals were $R = 0.061$, $R' = 0.066$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

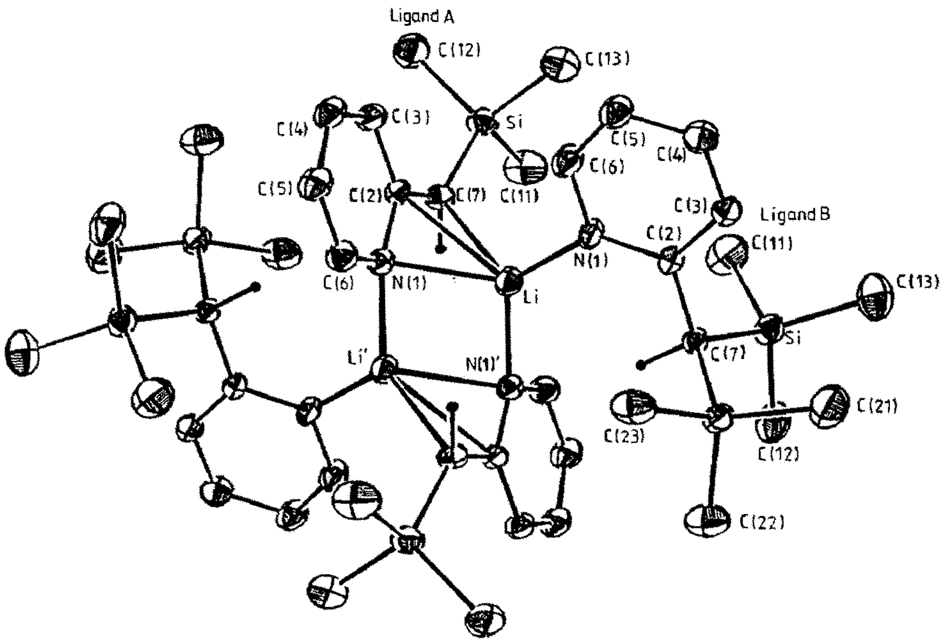

Fig. 1. Molecular projection of $[Li\{NC_5H_4\text{-}2\text{-}C(H)(SiMe_3)_2\}\{NC_5H_4\text{-}2\text{-}C(H)(SiMe_3)\}]_2$ (**1**) with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms shown. Selected bond distances and angles: Li–N(1)A 2.14(1), Li–N(1)A′ 2.06(1), Li–N(1)B 2.05(1), Li–C(7)A 2.39(1), Li–C(6)A 2.39(1), Li $\cdots$ Li 2.60(2) Å, N(1)A–Li–N(1)B 116.3(4), N(1)A′–Li–C(7)A 63.2(3), N(1)A–Li–N(1)A′ 103.5(4), N(1)A′–Li–C(7)A 104.5(3), N(1)A′–Li–N(1)B 129.5(4), C(7)A–Li–N(1)B 120.5(3), Li–N(1)A–Li′ 76.5(3)°.

ring, deviation 0.13 Å. Hydrogen *H* of R′*H* has an agostic interaction, Li $\cdots$ H 2.62 Å, consistent with its broad ^{1}H NMR chemical shift, line width 24 Hz, arising from close proximity to quadrupolar lithium; interactions of this type have been the subject of a recent theoretical treatment [7]. With *H* directed towards a metal centre, the associated bulky trimethylsilyl groups are directed to the periphery of the dimer thereby protecting *H* from metallation by excess LiBu^n. It is noteworthy that generation of **2** from **1** is associated with a transformation of the metal–R interaction from N-bridging/η^3-aza-allyl to bridging to both metal centres, exclusively through "anionic" N-centres of R groups possessing an exocyclic double bond [3]; concomitant loss of a monodentate for a bidentate ligand maintains formally eight valence electrons per metal centre.

A rationale for the greater acidity of R*H* than of R′*H* comes from structural data on organolithium compounds containing R$^-$ or R′$^-$. The former in **1**, **2**, $[\{Li(R)OEt_2\}_2]$ [3], and a related compound [5] have the *ipso*-carbon and associated atoms, including silicon, essentially coplanar with the pyridine ring, thus maximizing stabilization of charge by ring delocalization. However, in those containing R′$^-$ with no external constraints to delocalization, have the corresponding planes skewed by 38.2, **3**, and 40.9°, [Li(R′(R′*H*)] [3], in consequence of steric limitations in having two trimethylsilyl groups co-planar with the ring. Reduction in stabilization of charge by delocalization is seemingly responsible for the observed relative acidities. That is, diminution of negative hyperconjugation is overriding the polarizing power of the second silicon centre.

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References

1 M.F. Lappert, L.M. Engelhardt, C.L. Raston and A.H. White, J. Chem. Soc., Chem. Commun., (1982) 1323.
2 P. v. R. Schleyer, T. Clarke, A.J. Kos, G.W. Spitznagel, C. Rohde, D. Arad, K.N. Houk and N.G. Rondan, J. Am. Chem. Soc., 106 (1984) 6467.
3 R.I. Papasergio, B.W. Skelton, P. Twiss and A.H. White, J. Chem. Soc., Dalton Trans., (1990) 1161.
4 L.M. Engelhardt, W-P. Leung, C.L. Raston and A.H. White, J. Chem. Soc., Dalton Trans., (1985) 337.
5 R. Hacker, P.v.R. Schleyer, G. Reger, G. Muller and L. Brandsma, J. Organomet. Chem., 316 (1986) C4.
6 H. Dietrich, W. Mahdi and R. Knorr, J. Am. Chem. Soc., 108 (1986) 2462.
7 D. Barr, R. Snaith, R.E. Mulvey, and P.G. Perkins, Polyhedron, 7 (1988) 2119.