Synthesis of Pyridine Functionalised, Sterically Hindered Lithium and Copper(I) Alkyls; Crystal Structures of [{2-$(Me_3Si)_2C(M)C_5H_4N$}$_2$] (M = Li or Cu), Dimeric Compounds Free of Multicentre Bonding

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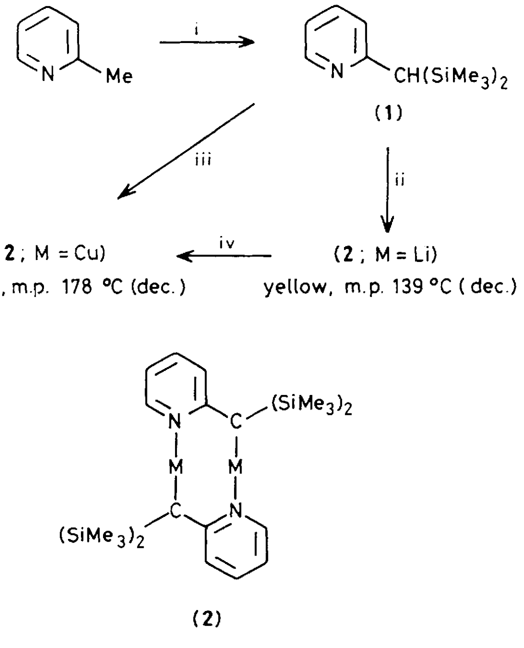
Reactions of 2-bis(trimethylsilyl)methylpyridine, (**1**), with LiBu^n in hexane–diethyl ether, and LiBu^n in tetrahydrofuran followed by CuCl, yields thermally robust binuclear complexes [{2-$(Me_3Si)C_2(M)C_5H_4N$}$_2$] for M = Li and M = Cu respectively in which the metal is not involved in electron deficient bonding, being bound by C_α of one ligand and the nitrogen of a centrosymmetrically related ligand and has a close metal contact [M · · · M 2.560(9) (Li) and 2.412(1) Å (Cu)].

We draw attention to a new sterically hindered alkyl ligand 2-$(Me_3Si)_2\bar{C}C_5H_4N$ (R^-), which is related to $(Me_3Si)_2CH^-$ and $(Me_3Si)_3C^-$, ligands capable of imparting unusual properties.[1] The structures of lithium and copper(I) derivatives of R^- are novel in being dimeric and free from multicentre bonding. In addition to the steric constraints imposed by R^-, it can in principle function as a four electron donor by chelation or bridging, as in the present examples, through the nitrogen, and it is stabilized with respect to β-hydrogen elimination.

Further noteworthy aspects of this work are (i) the ease of preparation of a crystalline, solvent-free lithium alkyl (**2**; M = Li), in high yield; (ii) its conversion into an analogous copper(I) compound (**2**; M = Cu); and (iii) the remarkable thermal stability of compounds (**2**), both being sublimable, at 160 °C (10^{-3} mmHg) with some decomposition for (**2**; M = Li).

Compounds (**2**) were prepared by the reactions in Scheme 1. The synthesis of lithium alkyls by metallation methods requires the presence of a lithium alkyl activating agent such as tmeda (tetramethylethylenediamine) or the use of diethyl ether–tetrahydrofuran (thf), as in the formation of $(Me_3Si)_2CHLi$[2] and $(Me_3Si)_3CLi$,[3] respectively. In the ligand precursor (**1**), the pyridine ring should provide the necessary activation intramolecularly, by analogy with the well known aryl-lithiation occurring *ortho* to tertiary amine groups,[4] but in n-hexane, Bu^{n}Li and (**1**) react to form a 1 : 1 adduct of (**1**) and the lithium alkyl LiR which is unaffected by additional Bu^{n}Li. In the presence of a catalytic amount of OEt_2 (*ca.* 0.2 equiv.), however, the 1 : 1 adduct reacts with further Bu^{n}Li to form (**2**; M = Li), a complex in which OEt_2 is not co-ordinated, unlike the *peri*-lithiation product of *N*,*N*-dimethyl-1-naphthylamine.[5] The compound which is isoelectronic to (**1**), $PhCH(SiMe_3)_2$, is unreactive towards Bu^{n}Li in hexane, and is not metallated at the tertiary carbon atom with Bu^{n}Li–(tmeda), even though this is the expected site of lithiation on the basis of relative thermodynamic acidities. The copper complex (**2**; M = Cu) was obtained by addition of CuCl to a solution of (**1**) and LiBu^n in hexane in the presence of thf, or, alternatively, from complex (**2**; M = Li) and CuCl in thf.



Scheme 1. *Reagents and conditions:* i, LiBu^n (1.7 M in n-C_6H_{14}) + tmeda, 2 h, 20 °C, then excess of $ClSiMe_3$ was added slowly; ii, LiBu^n (1.7 M in n-C_6H_{14}) + OEt_2, 1 h at 20 °C; iii, LiBu^n (1.7 M in n-C_6H_{14}) + thf, then CuCl, 1 h, 20 °C; iv, CuCl, thf, 1 h, 20 °C.

Single crystals of (**2**; M = Li) and (**2**; M = Cu) were obtained from hexane and their structures determined by *X*-ray crystallography. Compounds (**2**; M = Li) and (**2**; M = Cu) are composed of discrete dimers with one half as the asymmetric unit, the other being generated by an inversion centre.† Both are novel in being void of multicentre bonding, (see Figure 1). The C_α-metal non-bonding contacts are 2.619(7) and 3.111(4) Å for (**2**; M = Li) and (**2**; M = Cu) respectively.

In (**2**; M = Li) the Li–C_α distance is unexceptional whereas the Li–N bond is very short at 1.936(6) Å, *cf.* 2.10 Å for a typical Li–tertiary amine nitrogen distance as in [{*o*-$(Me_3Si)_2C_6H_4$}{Li(tmeda)}$_2$],[6] suggesting π bonding. This is further supported by the fact that the lithium atom is coplanar with the aromatic ring to which it is bound. The lithium is out of the plane defined by the other aromatic ring by 1.21 Å, leading to a step structure. Interestingly there are three Li–methyl-hydrogen contacts, at 2.23, 2.31, and 2.20 $(x,\bar{y},\bar{z})$ Å, similar to that found in [{(cyclohexyl)Li}$_6$].[7] The Li · · · Li distance, 2.560(9) Å, is comparable with those found in [{(MeLi)·½-

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† *Crystal data:* (**2**; M = Li), $C_{24}H_{44}Li_2N_2Si_4$, monoclinic, space group $P2_1/n$, a = 12.905(6), b = 9.983(4), c = 11.799(4) Å, β = 93.56(5)°, Z = 2. (**2**; M = Cu), $C_{24}H_{44}Cu_2N_2Si_4$, triclinic, space group $P\bar{1}$, a = 11.227(4), b = 9.153(3), c = 8.691(3) Å, α = 111.89(3), β = 100.12(3), γ = 100.59(3)°, Z = 1. Both structures were determined at room temperature, 295(1) K, from 2045 (**2**; M = Li), 1675 (**2**; M = Cu) independent 'observed' reflections (Mo-K_α radiation). R and R' values for (**2**; M = Li) and (**2**; M = Cu) are respectively 0.053, 0.056; 0.031, 0.036. 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.

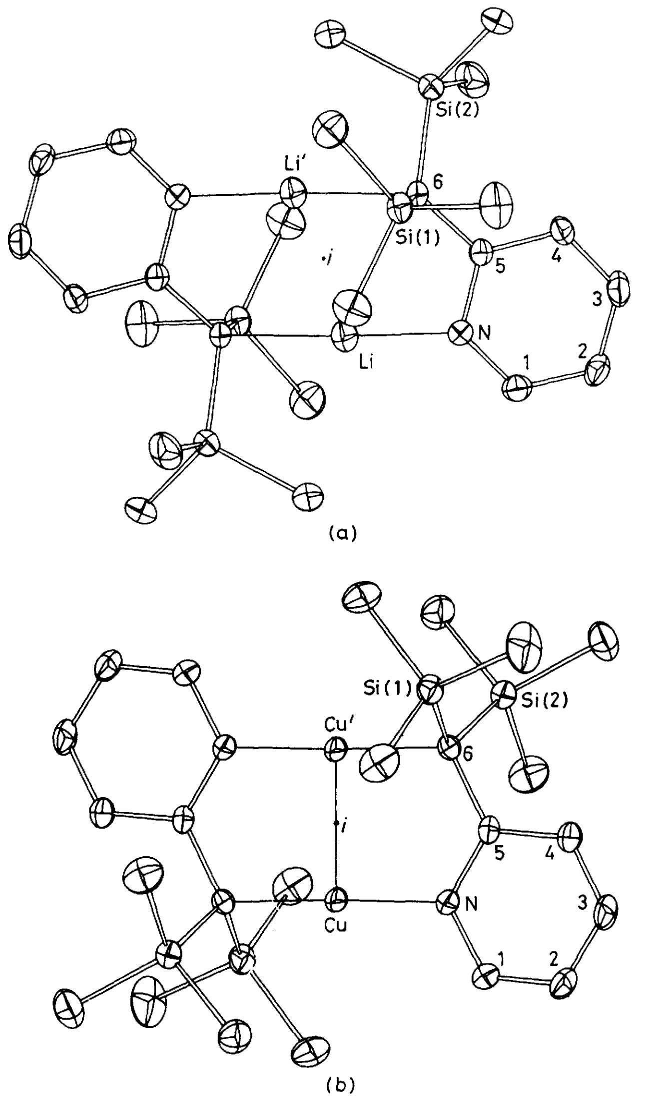

Figure 1. Molecular structures of [{2-$(Me_3Si)_2C(M)C_5H_4N$}$_2$], (**2**), M = Li (a) and M = Cu (b). Distances and angles defining the lithium [copper] environment are M–C(6′) 2.213(7) [1.950(4)], M–N 1.936(6) [1.910(3)], M–M′ 2.560(9) [2.412(1)] Å; C(6′)–M–N 146.9(4) [178.0(5)], M′–M–C(6′) 66.1(2) [90.4(1)], M′–M–N 104.4(3) [91.6(1)], M–N–C(1) 134.8(3) [119.8(2)], M–N–C(5) 104.9(3) [120.6(2)], M′–C(6)–Si(1) 104.6(2) [100.5(2)], M′–C(6)–Si(2) 88.8(2) [98.7(2)], M′–C(6)–C(5) 122.2(3)° [116.9(2)]. Non-hydrogen thermal ellipsoids are at the 20% probability level; projection is normal to the aromatic plane.

(tmeda)}$_4$], 2.561(6)—2.571(6) Å;[8] [{(C_6H_4-*o*-CH_2NMe_2)Li}$_4$], 2.49(1), 2.56(1) Å;[4] and [{*o*-Li(tmeda)C_6H_4}$_2$], 2.55(1) Å.[9]

In (**2**; M = Cu) the aromatic rings and the metal atoms are coplanar. The Cu · · · Cu distance, 2.412(1) Å, is similar to that found in the only other structurally authenticated copper(I) alkyl, [{(Me_3SiCH_2)Cu}$_4$], 2.417 Å,[10] whereas the Cu–C distance is much shorter [1.950(4), *cf.* 2.02 Å],[9] as would be expected from the electron deficient bonding in [{(Me_3SiCH_2)Cu}$_4$]. The Cu–C distance is more akin to that of [{$Me_2P(CH_2)_2$Cu}$_2$], 1.96 Å, in which, as for (**2**; M = Cu), the bonding is electron precise.[11] In the same compound Cu · · · Cu is longer at 2.843(3) Å, possibly reflecting the larger ligand 'bite' of $Me_2P(CH_2)_2^-$ compared to R^- and supporting the view that Cu · · · Cu bonding is not important. The disparity between M–C and M–N is less than in (**2**; M = Li), although the Cu–N distance is still unusually short at 1.910(3) Å, *cf.* 2.04 Å in [{ICu(pyridine)}$_4$].[12]

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References

1 *E.g.*, J. Jeffery, M. F. Lappert, and P. I. Riley, *J. Organomet. Chem.*, 1979, **181**, 25; C. Eaborn, N. Retta, and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1983, 905.
2 M. F. Lappert, L. M. Engelhardt, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 1323.
3 O. W. Steward and J. S. Johnson, *J. Organomet. Chem.*, 1973, **55**, 209.
4 J. T. B. H. Jastrzebski, G. van Koten, M. Konijn, and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 5490.
5 J. T. B. H. Jastrzebski, G. van Koten, K. Goubitz, C. Arlen, and M. Pfeffer, *J. Organomet. Chem.*, 1983, **246**, C75.
6 M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 14.
7 R. P. Zerger, W. E. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, 1974, **96**, 6048.
8 H. Koster, D. Thoennes, and E. Weiss, *J. Organomet. Chem.*, 1978, **160**, 1.
9 U. Schubert, W. Nengebauer, and P. von R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1982, 1184.
10 J. A. J. Jarvis, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1977, 999.
11 G. Nardin, L. Randaccio, and E. Zangrando, *J. Organomet. Chem.*, 1974, **74**, C23.
12 C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 2153.