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# Synthesis and molecular structures of copper(I) 1-azaallyls

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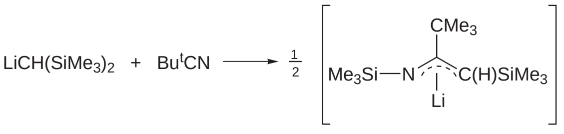
The reaction of the lithium 1-azaallyl $[\mathrm{Li}\{\mu\text{-}\mathrm{NRCBu^tC(H)R}\}]_2$ **1** with CuI gave the stable dimeric copper 1-azaallyl $[\{\mathrm{Cu}[\mu\text{-}\mathrm{NRCBu^tC(H)R}]\}_2]$ **2**, which upon treatment with $\mathrm{PPh_3}$ or a second equivalent of **1** gave the monomeric complex $[\mathrm{Cu}\{\mathrm{NRCBu^t{=}C(H)R}\}(\mathrm{PPh_3})]$ **3** or $[\mathrm{Li(dme)_3}][\mathrm{Cu}\{\mathrm{NRCBu^t{=}C(H)R}\}_2]$ **4**, respectively ($\mathrm{R = SiMe_3}$, dme = 1,2-dimethoxyethane). Each of the compounds **2**–**4** was fully characterised by multinuclear NMR spectroscopy, mass spectrometry, microanalysis and X-ray diffraction.

We recently reviewed initial progress on the synthesis, structures and reactions of alkali-metal α,ω-bis(trimethylsilyl)-1-azaallyls and -β-diketiminates, including their role as precursors for preparing unusual transition-metal and main group element complexes.[1] A major topic of this paper concerns reactions of the 1-azaallyllithium complex $[\mathrm{Li}(\mu\text{-}\mathrm{LL}')]_2$ **1** $[\mathrm{LL}' = \mathrm{NRCBu^tC(H)R}$, $\mathrm{R = SiMe_3}]$ in the context of copper(I) chemistry. Some of this work has been very briefly mentioned elsewhere.[2]

Complex **1**, readily obtained from $\mathrm{LiCHR_2}$ and $\mathrm{Bu^tCN}$ in diethyl ether or pentane under ambient conditions, equation (1),[3] has already successfully been used to obtain $[\mathrm{K(LL')}]_n$, *rac*-$[\overline{\mathrm{Zr(LL'}})_2\mathrm{Cl_2}]$,[3,4] $[\{\overline{\mathrm{Zr(LL'}})\mathrm{Cl_2}(\mu\text{-}\mathrm{Cl})\}_2]$,[4] *rac*-$\overline{\mathrm{Sn(LL'}})_2$,[5a] *rac*-$[\overline{\mathrm{Ln(LL'}})_2\mathrm{Cl(thf)}]$ (Ln = Ce or Nd),[6] *rac*-$[\overline{\mathrm{Sm(LL'}})_2\mathrm{I(thf)}]$, *rac*-$[\overline{\mathrm{Ln(LL'}})_2]$ (Ln = Sm[6] or Yb[6,7]), *rac*-$[\overline{\mathrm{Yb(LL'}})_2\mathrm{X}]$ (X = I or $\mathrm{OSO_2CF_3}$)[6] and *rac*-$[\{\overline{\mathrm{Th(LL'}})_2(\mu_3\text{-}\mathrm{Cl})(\mu\text{-}\mathrm{Cl})_2\mathrm{K(OEt_2)}\}_n]$ ($\mathrm{thf = OC_4H_8}$).[8] The majority of these have been structurally characterised. Among the general features of interest are: (i) the variety of bonding modes of $[\mathrm{LL'}]^-$, including $\eta^3$-chelating, $\eta^2$-bridging and $\eta^1$-enamido {see, *e.g.* tin(II) 1-azaallyls,[5a] and lithium or sodium[5b] derivatives of a related ligand $[\mathrm{Pr^nCHCBu^tNH}]^-$ in absence or presence of $\mathrm{PO(NMe_2)_3}$}; (ii) the lability of the $\mathrm{Me_3Si}$ substituents, and (iii) the chiral nature, at C-3, of the metal-bound $\eta^3$-1-azaallyl ligand. Thus, the bis(1-azaallyl)metal complexes have invariably been formed diastereoselectively as the *rac* isomers. The chemical properties of 1-azaallylmetal complexes relate to $[\mathrm{Li(LL')}]_2$ and its hydrolysis, ligand transfer, oxidation and a curious dyatropic rearrangement in the $\mathrm{CH_2Br_2}$–$\mathrm{LiBu^n}$ reaction;[2] while with $\mathrm{PCl_3}$ an $\mathrm{SiClMe_3}$ elimination reaction yielded $\mathrm{Cl\overline{PN(R')P(Cl)N}R'}$ $[\mathrm{R' = C(Bu^t){=}C(H)R}]$.[9]

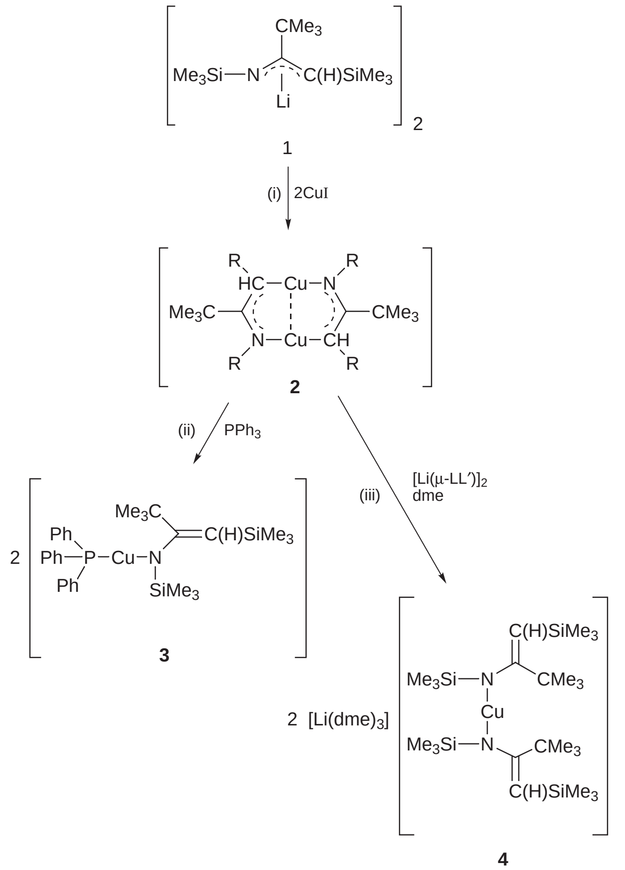


(1)

**1**

## Results and Discussion

The reaction of $[\mathrm{Li}(\mu\text{-}\mathrm{LL}')]_2$ **1** with 2 equivalents of CuI in a mixture of diethyl ether and pentane led in high yield to the copper(I) complex $[\{\mathrm{Cu}[\mu\text{-}\mathrm{NRCBu^tC(H)R}]\}_2]$ **2** [step (i) in Scheme 1]. Compound **2** was obtained solvent-free from pentane or a number of other solvents, including thf, as bright yellow crystals which were thermally stable under an argon atmosphere up to 150 °C and comparatively inert towards moist air (crystals turned black during *ca.* 30 min when exposed to air). Solutions of **2**, however, were much more sensitive and immediately precipitated copper metal upon contact with air. In the solid state, as well as in solution, **2** exhibited a clearly visible fluorescence. Similar observations on related complexes have recently attracted the interest of spectroscopists,[10] and experiments to explore the photo- and electro-chemistry of **2** and other complexes are currently in progress and will be published separately. The 1-azaallylcopper(I) complex **2** is dimeric in the solid state as was shown by X-ray diffraction (see below), while in the mass spectrum fragments corresponding to the mono- and di-meric formula units were observed.



**Scheme 1** Synthesis of the copper(I) complexes **2**, **3** and **4**: (i) $\mathrm{Et_2O}$–$\mathrm{C_5H_{12}}$, −45 °C to room temperature (r.t.); (ii) $\mathrm{Et_2O}$–$\mathrm{C_5H_{12}}$, −30 °C to r.t.; (iii) dme, r.t.

The addition of $\mathrm{PPh_3}$ or a second equivalent of $[\mathrm{Li}(\mu\text{-}\mathrm{LL}')]_2$ **1** to solutions of **2** in pentane led to an immediate decolorisation of the reaction mixture and, in the case of $\mathrm{PPh_3}$, colourless crystals of $[\mathrm{Cu}\{\mathrm{NRCBu^t{=}C(H)R}\}(\mathrm{PPh_3})]$ **3** were obtained [(ii) in Scheme 1] after subsequent cooling. The synthesis of the

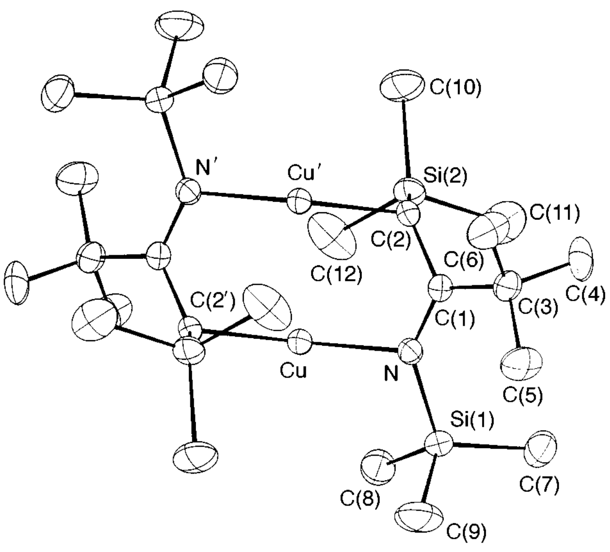


**Fig. 1** Molecular structure of complex **2**

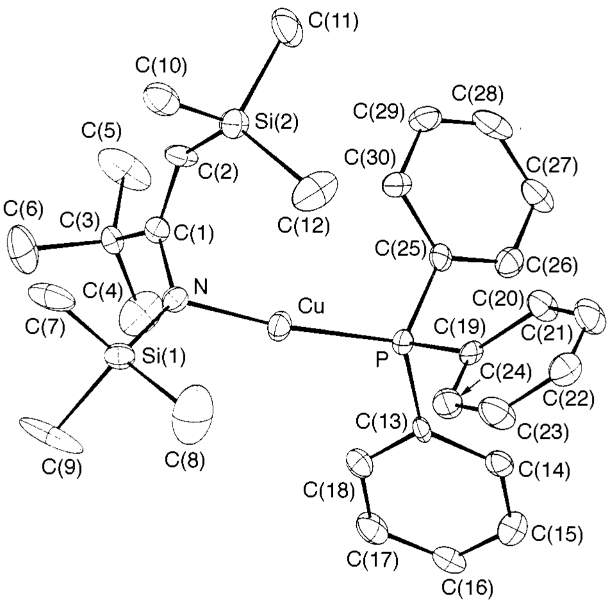


**Fig. 2** Molecular structure of complex **3**

cuprate $LiCu[NRCBu^tC(H)R]_2$ from **1** and **2**, however, proved to be less straightforward; upon cooling the reaction mixture, crystals only of the starting material **2** were observed. This indicates that there may be an equilibrium between **1** plus **2** and the cuprate $LiCu[NRCBu^tC(H)R]_2$, with **2** being the least soluble component and therefore crystallising first, thereby shifting the equilibrium towards the starting materials. We therefore chose to use a strong donor solvent, in the expectation that this would increase the stability of the cuprate by co-ordinating the lithium cation and forming a stable separated ion pair. Accordingly, a mixture of $[\{Cu(\mu\text{-}LL')\}_2]$ **2** and $[Li(\mu\text{-}LL')]_2$ **1** was redissolved in 1,2-dimethoxyethane (dme). After removal of the excess of solvent and recrystallisation from pentane, colourless crystals of $[Li(dme)_3][Cu\{NRCBu^t{=}C(H)R\}_2]$ **4** were obtained [(iii) in Scheme 1] in high yield.

Each of the complexes **3** and **4** was very soluble in pentane and showed a much reduced thermal stability and an increased air-sensitivity compared with **2**. One reason may be that their monomeric solid state structures are retained in solution and hence are less effective in shielding the central two-co-ordinate copper centre.

Attempts to obtain the silver analogue of **2**, **3** or **4**, from $[Li(\mu\text{-}LL')]_2$ and a variety of silver salts (AgI, $Ag[NO_3]$, $Ag[BF_4]$ or $Ag[OSO_2CF_3]$) and reaction conditions, have not been successful. Even at low temperature, each product appeared to decompose faster than it formed, with silver metal and the oxidised ligand $[RNCBu^tC(H)R]_2$ [2,6] as the only isolated products.

### Crystal structures of complexes 2, 3 and 4

The molecular structures of complexes **2**, **3** and **4** with the atom numbering schemes are illustrated in Figs. 1–3, respectively. Selected bond distances and angles are listed in Tables 1 and 2.

The crystalline compound $[\{Cu(\mu\text{-}LL')\}_2]$ **2** is a centrosymmetric dimer in which the $[LL']^-$ ligand acts in a bridging mode and thereby forms a distorted six-membered ring (excluding Cu atoms) in chair conformation, each ring substituent being *trans* to its neighbour (Fig. 1). With essentially equidistant Cu–C(2′) [1.943(6) Å] and Cu–N [1.921(5) Å] contacts and a C(2′)–Cu–N angle of 166.2(2)°, the central copper atoms are approximately linearly co-ordinated. The Cu · · · Cu′ distance of 2.499(2) Å is comparatively short; this is of interest in the light of theoretical discussions about $d^{10}$–$d^{10}$ closed-shell interactions between copper(I) centres;[11] although, as has been shown in related complexes, such close constants might be mainly determined by the constraints of the molecular geometry.[12] The short N–C(1) [1.309(8)] and long C(1)–C(2) [1.460(9) Å] distances correspond to double and single bonds, respectively, indicating that **2** is closer to being a copper iminoalkyl than an enamide. This is supported by NMR spectroscopic evidence (Table 3), see below. The crystalline lithium starting material **1**, in contrast, although also a dimer has more enamido character, as evident from the N–C and C–C distances of 1.402(7) and 1.36(1) Å, respectively.[3]

Dimeric structures are still comparatively rare for copper(I) alkyls, *cf.*[13] $[\{Cu(\mu\text{-}CH_2R)\}_4]$ having *l*(Cu–C) 2.02 Å, and have been observed only for bulky alkyls. The Cu–C and Cu–N distances and the angles around the metal as well as the general geometry of $[\{Cu(\mu\text{-}LL')\}_2]$ **2** resemble those of related dimeric compounds such as $[\{Cu(\mu\text{-}CH_2PMe_2CH_2)\}_2]$,[14] $[\{Cu(\mu\text{-}NRCPhNR)\}_2]$,[15] $[\{Cu[\mu\text{-}N(C_6H_4Me\text{-}4)NN(C_6H_4Me\text{-}4)\}_2]$,[11a] $[\{CuC_6H_3(Me\text{-}4)(CNCMe_2CH_2O\text{-}2)\}_2]$[16] and, in particular, $[\{Cu(\mu\text{-}NC_5H_4CR_2\text{-}2)\}_2]$.[12]

The crystalline phosphine adduct $[Cu(LL')(PPh_3)]$ **3** is a monomer (Fig. 2), the copper atom being approximately linearly co-ordinated by the N of the 1-azaallyl substituent and the P of the phosphine ligand [N–Cu–P 173.0(3)°]. In contrast to **2**, **3** is better described as an enamide than an iminoalkyl, as evident from the long C(1)–N distance of 1.38(1) Å and the short C(1)–C(2) bond of 1.35(1) Å. Copper amides are generally tetrameric: $[\{Cu(\mu\text{-}NMe_2)\}_4]$,[17] $[\{Cu(\mu\text{-}NC_4H_8)\}_4]$, $[\{Cu(\mu\text{-}NMeCH_2CH_2NMe_2)\}_4]$, $[\{Cu[\mu\text{-}N(CH_2CH_2NEt_2)_2]\}_4]$ and $[\{Cu(\mu\text{-}NEt_2)\}_4]$,[18] with Cu–N distances in the region of 1.90 Å.[17] It is interesting that each of these amides failed to react with $NEt_3$ or $PPh_3$; adducts were only obtained with a chelating phosphine, such as $Ph_2PCH_2PPh_2$ or $Ph_2P(CH_2)_2PPh_2$.[17] Monomeric phosphine complexes of copper amides are, we believe, unknown; some examples of monomeric copper(I) halide complexes are $[CuI\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}]$[19] or $[CuBr\{P(C_6H_2Me_3\text{-}2,4,6)_3\}]$.[20] The Cu–N and Cu–P bond distances in **3** of 1.840(8) and 2.145(3) Å, respectively, are very short compared with the above amido or halide complexes. The related copper(I) aryl $[Cu\{C_6H_3(C_6H_2Pr^i_3\text{-}2,4,6)_2\text{-}2,6\}(SMe_2)]$[21] also has very short Cu–C and Cu–S distances of 1.894(6) and 2.177(2) Å, respectively. Further examples of monomeric copper(I) complexes are $[Cu(SiPh_3)(PMe_3)_3]$,[22] $[CuPh\{(PPh_2CH_2)_3CMe\}]$[23] and $[Cu(\eta^5\text{-}C_5Me_5)\{C(PPh_3)_2\}]$.[24]

Owing to the strong disorder in the crystal structure of $[Li(dme)_3][Cu\{NRCBu^t{=}C(H)R\}_2]$ **4**, Fig. 4, bond distances and angles are not reliable. It is, however, clear that crystalline **4**, like **3**, is a monomer and consists of a separated ion pair (Fig. 3) similar to $[Li(thf)_4][Cu\{N(SiMePh_2)_2\}_2]$,[25] the only previous

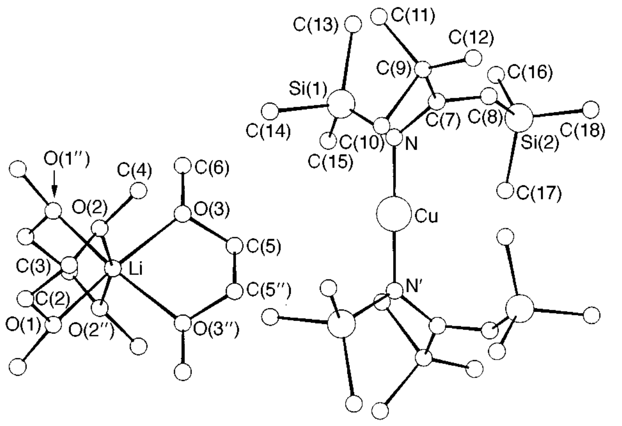


**Fig. 3** Molecular structure of complex **4**

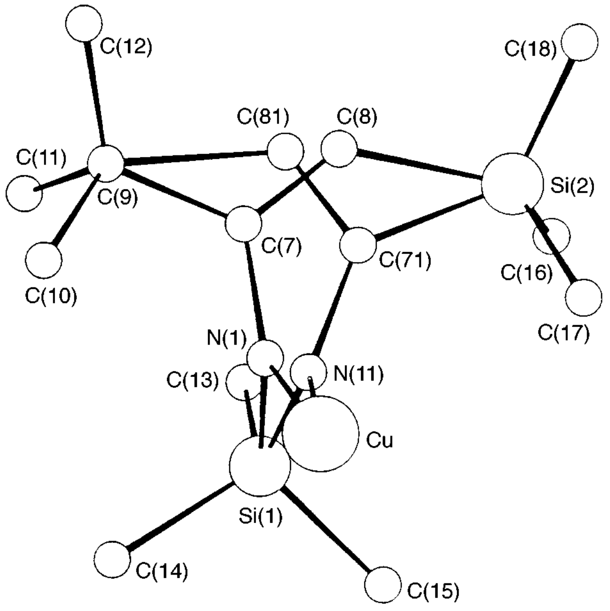


**Fig. 4** Illustration of the disorder of complex **4**

example of an amidocuprate(I). With bulky alkyl substituents, the similarly monomeric complexes [Li(thf)$_4$][Cu(CR$_3$)$_2$],[26] [Li(12-crown-4)][CuMe$_2$],[27] [Li(12-crown-4)][CuPh$_2$], [Li(12-crown-4)][CuBr{C(H)R$_2$}(PMe$_3$)] and [Cu{Ph$_2$P(CH$_2$)$_2$P-Ph$_2$}$_2$][Cu(C$_6$H$_2$Me$_3$-2,4,6)$_2$][28] having similar geometries have been reported.

### NMR spectra and solution behaviour

The NMR spectra of [{Cu(μ-LL′)}$_2$] **2** in [$^2$H$_6$]benzene or [$^2$H$_8$]toluene solution showed not only the expected signals for the ligand, but also that each line was accompanied closely by another of *ca.* 1/5 of the intensity. The ratio of the two sets of signals proved to be independent of repeated recrystallisation of **2** or of concentration differences in the NMR spectral samples, which makes a monomer–dimer equilibrium in solution unlikely. Spin saturation transfer studies showed that only at 100 °C in [$^2$H$_8$]toluene there was a spin transfer from one species to the other. This indicates the presence of two isomers: one **2a**, presumably the more abundant, may have each substituent in the dimer *trans* to its neighbour, while the other **2b** (probably thermodynamically the less favoured) has the trimethylsilyl substituents of one ligand in a staggered conformation relative to the other.

As we have already briefly mentioned in the context of tin(II) 1-azaallyls,[5] $^1$H and $^{13}$C NMR spectroscopy is a powerful tool for identifying different co-ordination modes of 1-azaallyl ligands in solution, especially in distinguishing between enamido- and iminoalkyl-metal complexes. For iminoalkyls, both $^1$H and $^{13}$C NMR spectral signals for CH are expected to be at low frequency, whereas the $^{13}$C signal of CN is at low frequency; the reverse situation prevails in the enamides. Table 3 summarises such data for compounds **1**–**4**; they confirm that in solution each compound retains its solid state structure.

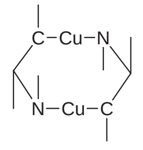
**Table 1** Selected bond distances (Å) and angles (°) of complex **2**

| | | | |
|---|---|---|---|
| Cu–N | 1.921(5) | Cu–C(2′) | 1.943(6) |
| Cu···Cu′ | 2.499(2) | Si(1)–N | 1.746(6) |
| Si(2)–C(2) | 1.872(7) | N–C(1) | 1.309(8) |
| C(1)–C(2) | 1.460(9) | C(1)–C(3) | 1.541(9) |
| N–Cu–C(2′) | 166.2(2) | C(1)–N–Si(1) | 139.5(5) |
| C(1)–N–Cu | 109.7(4) | Si(1)–N–Cu | 110.7(3) |
| N–C(1)–C(2) | 119.6(5) | N–C(1)–C(3) | 123.6(6) |
| C(2)–C(1)–C(3) | 116.8(5) | C(1)–C(2)–Si(2) | 116.4(5) |
| C(1)–C(2)–Cu′ | 114.0(4) | Si(2)–C(2)–Cu′ | 101.0(3) |

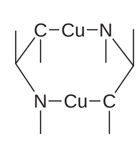
Primed atoms are related to unprimed ones by the symmetry transformation $-x$, $-y$, $-z$.

**Table 2** Selected bond distances (Å) and angles (°) of complex **3**

| | | | |
|---|---|---|---|
| Cu–N | 1.840(8) | Cu–P | 2.145(3) |
| P–C(13) | 1.80(1) | P–C(19) | 1.82(1) |
| P–C(25) | 1.81(1) | Si(1)–N | 1.72(1) |
| Si(2)–C(2) | 1.82(1) | N–C(1) | 1.38(1) |
| C(1)–C(2) | 1.35(1) | C(1)–C(3) | 1.57(1) |
| N–Cu–P | 173.0(3) | C(13)–P–C(19) | 105.1(4) |
| C(13)–P–C(25) | 104.5(5) | C(19)–P–C(25) | 106.0(4) |
| C(13)–P–Cu | 115.7(3) | C(19)–P–Cu | 111.8(4) |
| C(25)–P–Cu | 112.9(3) | C(1)–N–Si(1) | 131.3(7) |
| C(1)–N–Cu | 105.8(6) | Si(1)–N–Cu | 122.9(5) |
| C(2)–C(1)–N | 122.8(9) | C(2)–C(1)–C(3) | 120.2(9) |
| N–C(1)–C(3) | 116.8(8) | C(1)–C(2)–Si(2) | 131.1(8) |



**2a**



**2b**

## Experimental

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in C$_6$D$_6$ or C$_6$D$_5$CD$_3$ at 298 K using the following Bruker instruments: AC-P 250 ($^1$H, 250.1; $^{13}$C, 62.9; $^{31}$P 101.2), DPX 300 ($^1$H, 300.1) and AMX 500 ($^1$H, 500.1; $^{13}$C, 125.7 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of $^1$H and $^{13}$C spectra. The $^{31}$P NMR spectra were referenced externally to H$_3$PO$_4$. Unless otherwise stated, all NMR spectra other than $^1$H were proton-decoupled. Electron-impact mass spectra were from solid samples using a Kratos MS 80 RF instrument. Melting point were taken in sealed capillaries and are uncorrected.

### Preparations

**[{Cu[μ-NRCBu$^t$C(H)R]}$_2$] 2.** A solution of [Li(μ-LL′)]$_2$ **1** (3.64 g, 1.46 × 10$^{-2}$ mol) in pentane (30 cm$^3$) was added dropwise at −45 °C to a suspension of CuI (2.78 g, 2.92 × 10$^{-2}$ mol) in diethyl ether (100 cm$^3$). The reaction mixture was allowed to warm to room temperature. After stirring for 1.5 h a bright yellow solution with only a small amount of colourless precipitate was obtained, from which all volatiles were removed *in vacuo*. The residue was extracted with pentane (120 cm$^3$). The extract was filtered, the filtrate concentrated and cooled to −30 °C to give yellow crystals of **2** (3.4 g, 75%). A second crop of crystals (0.65 g, 14%) was obtained from the mother-liquor (Found: C, 47.2; H, 9.08; N, 4.58. $C_{12}H_{28}CuNSi_2$ requires C, 47.1; H, 9.22; N, 4.58%), m.p. 151 °C (decomp.). Mass spectrum [*m*/*z* (%)]: 612 (15, $[M_2]^+$), 545 (23, $[M_2 - Bu^t]^+$), 290 (30, $[M - Me]^+$) and 249 (55, $[M - Bu^t]^+$). $^1$H NMR ($C_6D_6$; values for minor isomer in parentheses): δ 0.35 (0.31) [s, $SiMe_3$], 0.44 (0.51) [s, $SiMe_3$], 1.20 (1.22) [s, $Bu^t$] and 3.11 (3.38) [s, CH]. $^{13}$C NMR ($C_6D_6$, $^1$H-coupled, values for minor isomer in $C_6D_5CD_3$ in parentheses): δ 3.9 (3.6) [q, $SiMe_3$, $^1J(^{13}C{-}^1H)$ 120.0], 5.3 (6.1) [q, $SiMe_3$, $^1J(^{13}C{-}^1H)$ 118.3], 30.7 (31.1) [q, $C(CH_3)_3$, $^1J(^{13}C{-}^1H)$ 126.3], 44.3 (44.6) [s, $C(CH_3)_3$], 48.1 (56.8) [d, CH, $^1J(^{13}C{-}^1H)$ 118.6 Hz] and 220.8 (219.6) [s, CN].

**[Cu{NRCBu$^t$=C(H)R}(PPh$_3$)] 3.** A solution of $PPh_3$ (0.71 g, $2.74 \times 10^{-3}$ mol) in $Et_2O$ (15 cm$^3$) was added slowly to a solution of complex **2** (0.84 g, $2.74 \times 10^{-3}$ mol) in pentane (40 cm$^3$) at −30 °C. After allowing the reaction mixture to warm to room temperature the nearly colourless solution was stirred for 1 h; the volatiles were then removed *in vacuo*. Extracting the residue with pentane (60 cm$^3$) and filtering the extract (removing a small amount of white precipitate) gave, after cooling the filtrate, the white solid **3** (1.35 g) which was slightly contaminated with free $PPh_3$. Recrystallisation from pentane yielded colourless crystals of **3** (1.16 g, 74%) (Found: C, 63.5; H, 7.58; N, 2.41. $C_{30}H_{43}CuNPSi_2$ requires C, 63.4; H, 7.63; N, 2.46%), m.p. 110 °C (decomp.), mass spectrum: only of decomposition products. $^1$H NMR ($C_6D_6$): δ 0.47 (s, $SiMe_3$), 0.58 (s, $SiMe_3$), 1.46 (s, $Bu^t$), 5.05 (s, CH), 6.97 (m, Ph, 3 H) and 7.45 (m, Ph, 2 H). $^{31}$P NMR ($C_6D_6$): δ 12.7. $^{13}$C NMR ($C_6D_6$, $^1$H coupled): δ 2.3 [q, $SiMe_3$, $^1J(^{13}C{-}^1H)$ 118.2], 5.05 [q, $SiMe_3$, $^1J(^{13}C{-}^1H)$ 116.7], 31.8 [s, $C(CH_3)_3$ $^1J(^{13}C{-}^1H)$ 124.9], 39.5 [s, $C(CH_3)_3$], 101.9 [s, CH, $^1J(^{13}C{-}^1H)$ 129.7], 129.2 [dd, *m*-C, $^1J(^{13}C{-}^1H)$ 152.8, $^3J(^{13}C{-}^{31}P)$ 10.0], 130.8 [d, *p*-C, $^1J(^{13}C{-}^1H)$ 161.3], 134.0 [dd, *o*-C, $^1J(^{13}C{-}^1H)$ 158.3, $^2J(^{13}C{-}^{31}P)$ 15.2 Hz], *ipso*-C not observed, 177.5 (s, CN).

**Table 3** Some comparative NMR chemical shift (δ) and bond length (Å) data for complexes **1**–**4**

| Complex | δ $^1$H(CH) | δ $^{13}$C(CN) | δ $^{13}$C(*C*C) | C–N/Å | C–C/Å |
|---|---|---|---|---|---|
| **1**[3] | 4.54 | 170.8 | 93.7 | 1.40(1) | 1.36(1) |
| **2** | 3.11 | 220.8 | 48.1 | 1.31(1) | 1.46(1) |
| **3** | 5.05 | 177.5 | 101.9 | 1.38(1) | 1.35(1) |
| **4** | 4.83 | 182.3 | 97.1 | [1.44(2)]* | [1.28(2)]* |

* These data may not be reliable (see Table 4).

**[Li(dme)$_3$][Cu{NRCBu$^t$=C(H)R}$_2$] 4.** A solution of complex **1** (0.80 g, $1.93 \times 10^{-3}$ mol) in pentane (10 cm$^3$) was slowly added to a solution of **2** (0.98 g, $1.93 \times 10^{-3}$ mol) in pentane (30 cm$^3$) at room temperature, the reaction mixture changing from yellow to colourless. The mixture was stirred for 2 h, concentrated and cooled whereupon yellow crystals of **2** precipitated. Without isolating the crystals, volatiles were removed *in vacuo*, the residue was dissolved in dme (5 cm$^3$), the excess of solvent removed *in vacuo* and the white residue recrystallised from pentane. Upon cooling, colourless crystals of **4** (0.73 g, 31%) were obtained. A second crop of crystals (0.63 g, 27%) was isolated from the mother-liquid (Found: C, 52.5; H, 10.09; N, 3.42. $C_{36}H_{86}CuLiN_2O_6Si_4$ requires C, 52.4; H, 10.50; N, 3.39%), m.p. 94 °C (decomp.). Mass spectrum [*m*/*z* (%)]: 497 {40, $[LiCu(LL')_2 - Bu^t]^+$} and 187 {42, $[Li(dme)_2]^+$}. $^1$H NMR ($C_6D_6$–$C_5D_5N$): δ 0.57 (s, $SiMe_3$), 0.65 (s, $SiMe_3$), 1.64 (s, $Bu^t$), 3.08 (s, OMe), 3.30 (s, $OCH_2$) and 4.83 (s, CH). $^{13}$C NMR ($C_6D_6$–$C_5D_5N$): δ 2.6 (s, $SiMe_3$), 5.5 (s, $SiMe_3$), 33.0 [s, $C(CH_3)_3$], 40.7 [s, $C(CH_3)_3$], 58.6 (s, $OCH_2$), 72.0 (s, OMe), 97.1 (s, CH) and 182.3 (s, CN).

## Crystallography

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromatic Mo-Kα radiation (λ 0.710 73 Å). For complex **2** the crystals were sealed in a Lindemann capillary under argon, whilst for **3** and **4** the crystal was enclosed in an oil drop and frozen in a stream of cold nitrogen gas. Cell dimensions were calculated from the setting angles for 25 reflections

**Table 4** Crystallographic data for compounds **2**, **3** and **4**

| | **2** | **3** | **4** |
|---|---|---|---|
| Formula | $C_{24}H_{56}Cu_2N_2Si_4$ | $C_{30}H_{43}CuNPSi_2$ | $C_{36}H_{86}CuLiN_2O_6Si_4$ |
| *M* | 612.2 | 568.3 | 825.9 |
| *T*/K | 293(2) | 173(2) | 173(2) |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ (no. 2) | $P2_1/n$ (no. 14) | $P2/c$ (no. 13) |
| *a*/Å | 9.210(4) | 12.135(4) | 9.653(12) |
| *b*/Å | 9.412(3) | 14.805(5) | 14.164(14) |
| *c*/Å | 11.624(4) | 17.896(5) | 18.277(15) |
| α/° | 102.83(3) | | |
| β/° | 91.97(3) | 105.40(3) | 94.93(9) |
| γ/° | 118.86(3) | | |
| *U*/Å$^3$ | 848.5(5) | 3100(2) | 2490(5) |
| *Z* | 1 | 4 | 2 |
| $D_c$/Mg m$^{-3}$ | 1.20 | 1.22 | 1.10 |
| *F*(000) | 328 | 1208 | 904 |
| μ/mm$^{-1}$ | 1.41 | 0.85 | 0.57 |
| Crystal size/mm | 0.25 × 0.20 × 0.05 | 0.5 × 0.4 × 0.2 | 0.4 × 0.4 × 0.4 |
| θ Range/° | 2 to 25 | 2 to 25 | 2 to 23 |
| Index ranges | $0 \le h \le 10, -11 \le k \le 9, -13 \le l \le 13$ | $0 \le h \le 14, 0 \le k \le 17, -21 \le l \le 20$ | $0 \le h \le 10, 0 \le k \le 15, -20 \le l \le 20$ |
| Reflections collected | 2979 | 5708 | 3681 |
| Independent reflections | 2979 | 5446 ($R_{int}$ = 0.149) | 3456 ($R_{int}$ = 0.107) |
| Reflections with $I > 2\sigma(I)$ | 2012 | 2506 | 1654 |
| No. variables | 145 | 316 | 255 |
| $R1$ [$I > 2\sigma(I)$] | 0.061 | 0.101 | 0.098 |
| $wR2$ (all data) | 0.191 | 0.286 | 0.323 |
| Largest difference peak/e Å$^{-3}$ | 0.66 | 1.22 | 0.50 |
| Absorption correction from ψ scans | $T_{max}$ = 1.00, $T_{min}$ = 0.75 | — | — |
| Maximum shift/e.s.d. | 0.001 | 0.006 | 0.25 |

with 7 < θ < 10°. Intensities were measured by an ω–2θ scan. Corrections were made for Lorentz-polarisation effects and also for **2** only for absorption by ψ scans. There was no crystal decay as measured by two standard reflections. Positions of non-hydrogen atoms were derived by direct methods using SHELXS 86[29] and refined on $F^2$ with anisotropic thermal parameters for non-hydrogen atoms and H atoms in riding mode, by full-matrix least squares using SHELXL 93.[30] Unfortunately **4** is disordered with the anion being disordered in a 0.57 : 0.43 ratio between two conformations in which there are resolved sites for C(7), C(8) and N, a common $SiMe_3$ group on N, and the other $SiMe_3$ group and the $Bu^t$ group overlapping (Fig. 4). Further details are in Table 4.

CCDC reference number 186/950.

See http://www.rsc.org/suppdata/dt/1998/1619/ for crystallographic files in .cif format.

## Acknowledgements

We are grateful to the EC for the award of a fellowship (to M. L.) and to the EPSRC for other support.

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*Received* 12*th February* 1998; *Paper* 8/01232F