

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

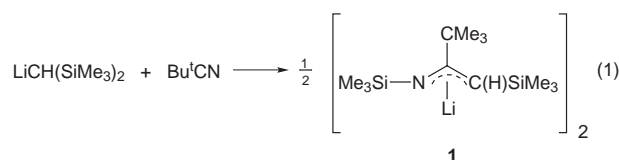
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The reaction of the lithium 1-azaallyl $[\text{Li}\{\mu\text{-NRCBu}^t\text{C(H)R}\}]_2$ **1** with CuI gave the stable dimeric copper 1-azaallyl $[\{\text{Cu}\{\mu\text{-NRCBu}^t\text{C(H)R}\}]_2$ **2**, which upon treatment with PPh_3 or a second equivalent of **1** gave the monomeric complex $[\text{Cu}\{\text{NRCBu}^t\text{C(H)R}\}(\text{PPh}_3)]$ **3** or $[\text{Li}(\text{dme})_3][\text{Cu}\{\text{NRCBu}^t\text{C(H)R}\}]$ **4**, respectively ($\text{R} = \text{SiMe}_3$, $\text{dme} = 1,2\text{-dimethoxyethane}$). 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 $[\text{Li}(\mu\text{-LL}')_2]$ **1** [$\text{LL}' = \text{NRCBu}^t\text{C(H)R}$, $\text{R} = \text{SiMe}_3$] in the context of copper(I) chemistry. Some of this work has been very briefly mentioned elsewhere.²

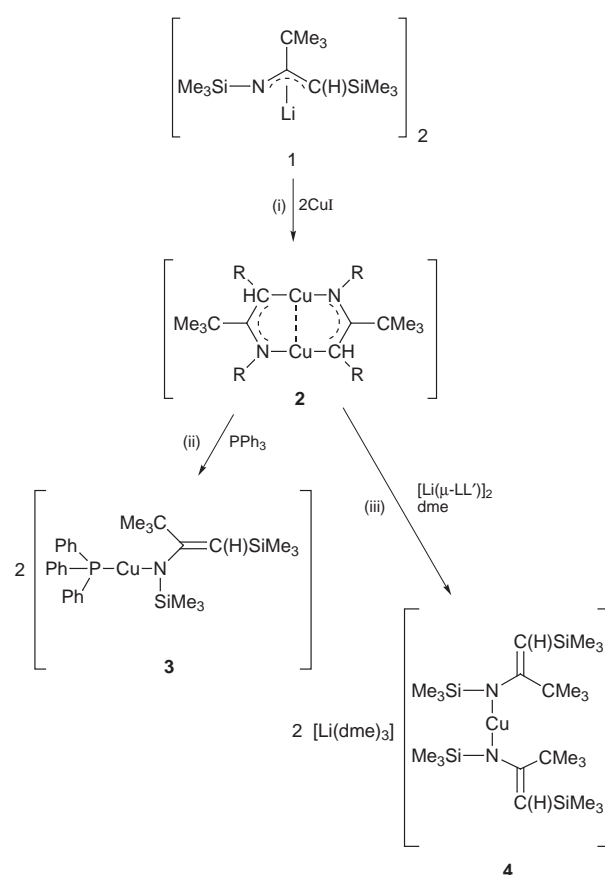
Complex **1**, readily obtained from LiCHR_2 and Bu^tCN in diethyl ether or pentane under ambient conditions, equation (1),³ has already successfully been used to obtain $[\text{K}(\text{LL}')_n]$, *rac*-



$[\text{Zr}(\text{LL}')_2\text{Cl}_2]$,^{3,4} $[\{\text{Zr}(\text{LL}')\text{Cl}_2(\mu\text{-Cl})\}_2]$,⁴ *rac*- $[\text{Sn}(\text{LL}')_2]$,^{5a} *rac*- $[\text{Ln}(\text{LL}')_2\text{Cl}(\text{thf})]$ ($\text{Ln} = \text{Ce}$ or Nd),⁶ *rac*- $[\text{Sm}(\text{LL}')_2\text{I}(\text{thf})]$, *rac*- $[\text{Ln}(\text{LL}')_2]$ ($\text{Ln} = \text{Sm}$ ⁶ or Yb ^{6,7}), *rac*- $[\text{Yb}(\text{LL}')_2\text{X}]$ ($\text{X} = \text{I}$ or OSO_2CF_3)⁶ and *rac*- $[\{\text{Th}(\text{LL}')_2(\mu_3\text{-Cl})(\mu\text{-Cl})_2\text{K}(\text{OEt}_2)_n\}]$ ($\text{thf} = \text{OC}_4\text{H}_8$).⁸ The majority of these have been structurally characterised. Among the general features of interest are: (i) the variety of bonding modes of $[\text{LL}']^-$, including η^3 -chelating, η^2 -bridging and η^1 -enamido {see, e.g. tin(II) 1-azaallyls,^{5a} and lithium or sodium^{5b} derivatives of a related ligand $[\text{Pr}^n\text{CH-CBu}^t\text{NH}]^-$ in absence or presence of $\text{PO}(\text{NMe}_2)_3$ }; (ii) the lability of the Me_3Si substituents, and (iii) the chiral nature, at C-3, of the metal-bound η^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 $[\text{Li}(\text{LL}')_2]$ and its hydrolysis, ligand transfer, oxidation and a curious dyatropic rearrangement in the $\text{CH}_2\text{Br}_2\text{-LiBu}^n$ reaction;² while with PCl_3 an SiClMe_3 elimination reaction yielded $\text{ClP}(\text{R}')\text{P}(\text{Cl})\text{NR}'$ [$\text{R}' = \text{C}(\text{Bu}^t)=\text{C}(\text{H})\text{R}$].⁹

Results and Discussion

The reaction of $[\text{Li}(\mu\text{-LL}')_2]$ **1** with 2 equivalents of CuI in a mixture of diethyl ether and pentane led in high yield to the copper(I) complex $[\{\text{Cu}\{\mu\text{-NRCBu}^t\text{C(H)R}\}]_2$ **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



Scheme 1 Synthesis of the copper(I) complexes **2**, **3** and **4**: (i) $\text{Et}_2\text{O-C}_5\text{H}_{12}$, -45°C to room temperature (r.t.); (ii) $\text{Et}_2\text{O-C}_5\text{H}_{12}$, -30°C to r.t.; (iii) dme , r.t.

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.

The addition of PPh_3 or a second equivalent of $[\text{Li}(\mu\text{-LL}')_2]$ **1** to solutions of **2** in pentane led to an immediate decolorisation of the reaction mixture and, in the case of PPh_3 , colourless crystals of $[\text{Cu}\{\text{NRCBu}^t\text{C(H)R}\}(\text{PPh}_3)]$ **3** were obtained [(ii) in Scheme 1] after subsequent cooling. The synthesis of the

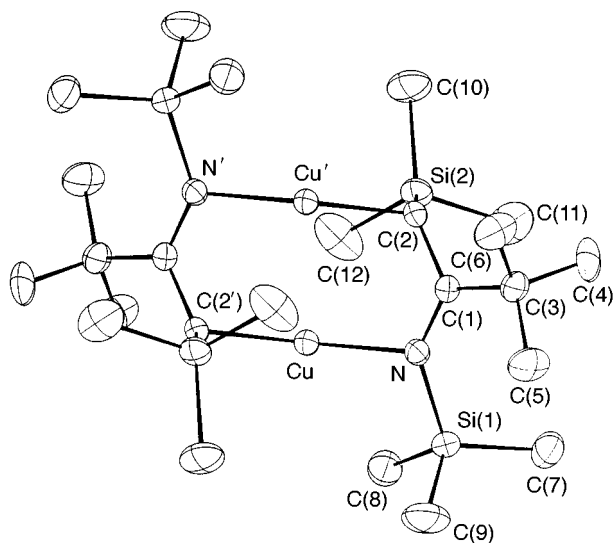


Fig. 1 Molecular structure of complex 2

cuprate $\text{LiCu}[\text{NRCBu}^t\text{C}(\text{H})\text{R}]_2$ 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 $\text{LiCu}[\text{NRCBu}^t\text{C}(\text{H})\text{R}]_2$, 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 $[\{\text{Cu}(\mu\text{-LL}')\}_2]$ **2** and $[\text{Li}(\mu\text{-LL}')]$ **1** was redissolved in 1,2-dimethoxyethane (dme). After removal of the excess of solvent and recrystallisation from pentane, colourless crystals of $[\text{Li}(\text{dme})_3][\text{Cu}\{\text{NRCBu}^t\text{C}(\text{H})\text{R}\}_2]$ **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 $[\text{Li}(\mu\text{-LL}')_2]$ and a variety of silver salts (AgI , $\text{Ag}[\text{NO}_3]$, $\text{Ag}[\text{BF}_4]$ or $\text{Ag}[\text{OSO}_2\text{CF}_3]$) 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 $[\text{RNRCBu}^t\text{C}(\text{H})\text{R}]_2$ 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 $[\{\text{Cu}(\mu\text{-LL}')\}_2]$ **2** is a centrosymmetric dimer in which the $[\text{LL}']^-$ 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 $166.2(2)^\circ$, 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

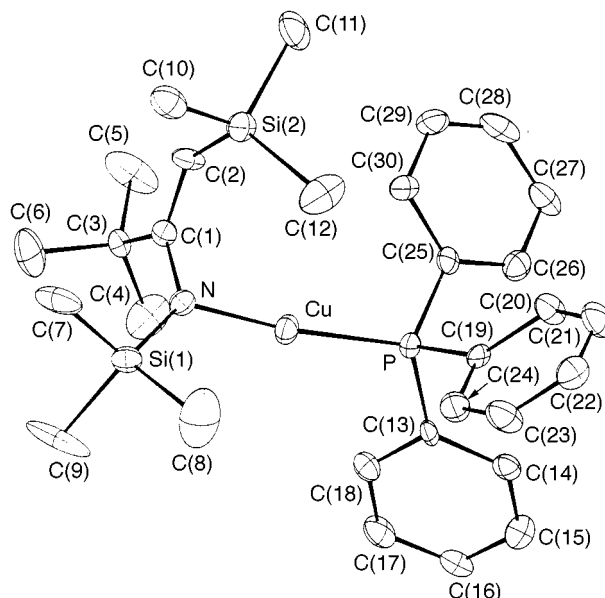


Fig. 2 Molecular structure of complex 3

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 $[\{\text{Cu}(\mu\text{-CH}_2\text{R})\}_2]$ having $l(\text{Cu}-\text{C})$ 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 $[\{\text{Cu}(\mu\text{-LL}')\}_2]$ **2** resemble those of related dimeric compounds such as $[\{\text{Cu}(\mu\text{-CH}_2\text{PMe}_2\text{CH}_2)\}_2]$,¹⁴ $[\{\text{Cu}(\mu\text{-NRCPhNR})\}_2]$,¹⁵ $[\{\text{Cu}[\mu\text{-N}(\text{C}_6\text{H}_4\text{Me-4})\text{NN}(\text{C}_6\text{H}_4\text{Me-4})]\}_2]$,^{11a} $[\{\text{Cu}(\mu\text{-NC}_6\text{H}_3(\text{Me-4})(\text{CNCMe}_2\text{CH}_2\text{O-2}))\}_2]$ ¹⁶ and, in particular, $[\{\text{Cu}(\mu\text{-NC}_5\text{H}_4\text{CR}_2\text{-2})\}_2]$.¹²

The crystalline phosphine adduct $[\text{Cu}(\text{LL}')(\text{PPh}_3)]$ **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 $173.0(3)^\circ$]. 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: $[\{\text{Cu}(\mu\text{-NMe}_2)\}_4]$,¹⁷ $[\{\text{Cu}(\mu\text{-NC}_4\text{H}_8)\}_4]$, $[\{\text{Cu}(\mu\text{-NMeCH}_2\text{CH}_2\text{NMe}_2)\}_4]$, $[\{\text{Cu}[\mu\text{-N}(\text{CH}_2\text{CH}_2\text{NEt}_2)]_4\}]$ and $[\{\text{Cu}(\mu\text{-NEt}_2)\}_4]$,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 $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ or $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$.¹⁷ Monomeric phosphine complexes of copper amides are, we believe, unknown; some examples of monomeric copper(i) halide complexes are $[\text{CuI}\{\text{P}[\text{C}_6\text{H}_2(\text{OMe})_3\text{-2,4,6}]\}_3]$ ¹⁹ or $[\text{CuBr}\{\text{P}[\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}]\}_3]$.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 $[\text{Cu}\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}_3^i\text{-2,4,6})_2\text{-2,6}-(\text{SMe}_2)\}_2]$ 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 $[\text{Cu}(\text{SiPh}_3)(\text{PMe}_3)_3]$,²² $[\text{CuPh}\{\text{P}(\text{Ph}_2\text{CH}_2)_3\text{CMe}\}]$ ²³ and $[\text{Cu}(\eta^5\text{-C}_5\text{Me}_5)\{\text{C}(\text{PPh}_3)_2\}]$.²⁴

Owing to the strong disorder in the crystal structure of $[\text{Li}(\text{dme})_3][\text{Cu}\{\text{NRCBu}^t\text{C}(\text{H})\text{R}\}_2]$ **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 $[\text{Li}(\text{thf})_4][\text{Cu}\{\text{N}(\text{SiMePh}_2)_2\}_2]$,²⁵ the only previous

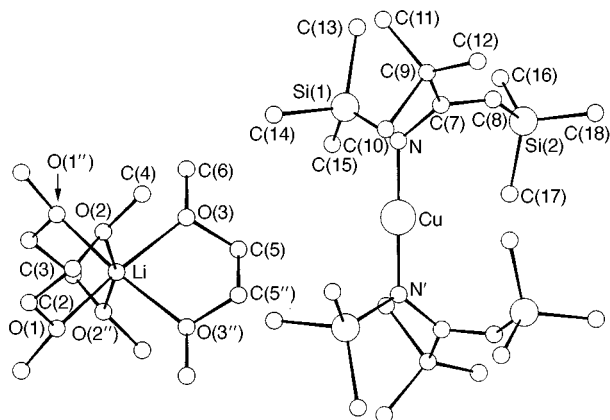


Fig. 3 Molecular structure of complex 4

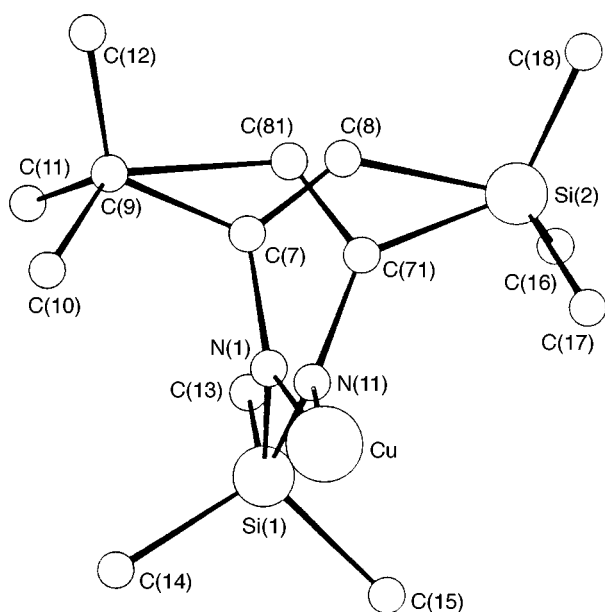


Fig. 4 Illustration of the disorder of complex 4

example of an amidocuprate(1). With bulky alkyl substituents, the similarly monomeric complexes $[\text{Li}(\text{thf})_4][\text{Cu}(\text{CR}_3)_2]$,²⁶ $[\text{Li}(12\text{-crown-4})][\text{CuMe}_2]$,²⁷ $[\text{Li}(12\text{-crown-4})][\text{CuPh}_2]$, $[\text{Li}(12\text{-crown-4})][\text{CuBr}\{\text{C}(\text{H})\text{R}_2\}(\text{PMe}_3)]$ and $[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph}_2)_2\}][\text{Cu}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2]$ ²⁸ having similar geometries have been reported.

NMR spectra and solution behaviour

The NMR spectra of $[\{\text{Cu}(\mu\text{-LL}')\}_2]$ **2** in $[\text{D}_6]\text{benzene}$ or $[\text{D}_8]\text{toluene}$ 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 $[\text{D}_8]\text{toluene}$ 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 ^1H and ^{13}C NMR spectroscopy is a powerful tool for identifying different co-ordination modes of 1-azaallyl lig-

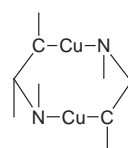
Table 1 Selected bond distances (Å) and angles (°) of complex 2

| | | | |
|----------------|----------|-----------------|----------|
| 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) |

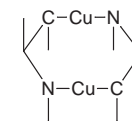
Primed atoms are related to unprimed ones by the symmetry transformation $-x, -y, -z$.

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

ands in solution, especially in distinguishing between enamido- and iminoalkyl-metal complexes. For iminoalkyls, both ^1H 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.

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_6D_6 or $\text{C}_6\text{D}_5\text{CD}_3$ at 298 K using the following Bruker instruments: AC-P 250 (^1H , 250.1; ^{13}C , 62.9; ^{31}P 101.2), DPX 300 (^1H , 300.1) and AMX 500 (^1H , 500.1; ^{13}C , 125.7 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of ^1H and ^{13}C spectra. The ^{31}P NMR spectra were referenced externally to H_3PO_4 . Unless otherwise stated, all NMR spectra other than ^1H 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'C(H)R]\}_2] **2**. A solution of $[\text{Li}(\mu\text{-LL}')_2]$ **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 precipi-

tate was obtained, from which all volatiles were removed *in vacuo*. The residue was extracted with pentane (120 cm³). 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. C₁₂H₂₈CuNSi₂ requires C, 47.1; H, 9.22; N, 4.58%), m.p. 151 °C (decomp.). Mass spectrum [*m/z* (%): 612 (15, [M₂]⁺), 545 (23, [M₂ - Bu]⁺), 290 (30, [M - Me]⁺) and 249 (55, [M - Bu]⁺). ¹H NMR (C₆D₆; values for minor isomer in parentheses): δ 0.35 (0.31) [s, SiMe₃], 0.44 (0.51) [s, SiMe₃], 1.20 (1.22) [s, Bu] and 3.11 (3.38) [s, CH]. ¹³C NMR (C₆D₆; ¹H-coupled, values for minor isomer in C₆D₅CD₃ in parentheses): δ 3.9 (3.6) [q, SiMe₃, ¹J(¹³C-¹H) 120.0], 5.3 (6.1) [q, SiMe₃, ¹J(¹³C-¹H) 118.3], 30.7 (31.1) [q, C(CH₃)₃, ¹J(¹³C-¹H) 126.3], 44.3 (44.6) [s, C(CH₃)₃], 48.1 (56.8) [d, CH, ¹J(¹³C-¹H) 118.6 Hz] and 220.8 (219.6) [s, CN].

[Cu{NRCBu^t=C(H)R}(PPh₃)] 3. A solution of PPh₃ (0.71 g, 2.74 × 10⁻³ mol) in Et₂O (15 cm³) was added slowly to a solution of complex **2** (0.84 g, 2.74 × 10⁻³ mol) in pentane (40 cm³) 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 cm³) 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 PPh₃. Recrystallisation from pentane yielded colourless crystals of **3** (1.16 g, 74%) (Found: C, 63.5; H, 7.58; N, 2.41. C₃₀H₄₃CuNPSi₂ requires C, 63.4; H, 7.63; N, 2.46%),

m.p. 110 °C (decomp.), mass spectrum: only of decomposition products. ¹H NMR (C₆D₆): δ 0.47 (s, SiMe₃), 0.58 (s, SiMe₃), 1.46 (s, Bu^t), 5.05 (s, CH), 6.97 (m, Ph, 3 H) and 7.45 (m, Ph, 2 H). ³¹P NMR (C₆D₆): δ 12.7. ¹³C NMR (C₆D₆; ¹H coupled): δ 2.3 [q, SiMe₃, ¹J(¹³C-¹H) 118.2], 5.05 [q, SiMe₃, ¹J(¹³C-¹H) 116.7], 31.8 [s, C(CH₃)₃, ¹J(¹³C-¹H) 124.9], 39.5 [s, C(CH₃)₃], 101.9 [s, CH, ¹J(¹³C-¹H) 129.7], 129.2 [dd, *m*-C, ¹J(¹³C-¹H) 152.8, ³J(¹³C-³¹P) 10.0], 130.8 [d, *p*-C, ¹J(¹³C-¹H) 161.3], 134.0 [dd, *o*-C, ¹J(¹³C-¹H) 158.3, ²J(¹³C-³¹P) 15.2 Hz], *ipso*-C not observed, 177.5 (s, CN).

[Li(dme)₃][Cu{NRCBu^t=C(H)R}₂] 4. A solution of complex **1** (0.80 g, 1.93 × 10⁻³ mol) in pentane (10 cm³) was slowly added to a solution of **2** (0.98 g, 1.93 × 10⁻³ mol) in pentane (30 cm³) 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 cm³), 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. C₃₆H₈₆CuLiN₂O₆Si₄ 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]⁺} and 187 {42, [Li(dme)₂]⁺}. ¹H NMR (C₆D₆-C₅D₅N): δ 0.57 (s, SiMe₃), 0.65 (s, SiMe₃), 1.64 (s, Bu^t), 3.08 (s, OMe), 3.30 (s, OCH₂) and 4.83 (s, CH). ¹³C NMR (C₆D₆-C₅D₅N): δ 2.6 (s, SiMe₃), 5.5 (s, SiMe₃), 33.0 [s, C(CH₃)₃], 40.7 [s, C(CH₃)₃], 58.6 (s, OCH₂), 72.0 (s, OMe), 97.1 (s, CH) and 182.3 (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(CC) | 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).

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 ₂ N ₂ Si ₄ | C ₃₀ H ₄₃ CuNPSi ₂ | C ₃₆ H ₈₆ CuLiN ₂ O ₆ Si ₄ |
| <i>M</i> | 612.2 | 568.3 | 825.9 |
| <i>T</i> /K | 293(2) | 173(2) | 173(2) |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> 2/ <i>c</i> (no. 13) |
| <i>a</i> /Å | 9.210(4) | 12.135(4) | 9.653(12) |
| <i>b</i> /Å | 9.412(3) | 14.805(5) | 14.164(14) |
| <i>c</i> /Å | 11.624(4) | 17.896(5) | 18.277(15) |
| <i>a</i> /° | 102.83(3) | | |
| <i>β</i> /° | 91.97(3) | 105.40(3) | 94.93(9) |
| <i>γ</i> /° | 118.86(3) | | |
| <i>U</i> /Å ³ | 848.5(5) | 3100(2) | 2490(5) |
| <i>Z</i> | 1 | 4 | 2 |
| <i>D_c</i> /Mg m ⁻³ | 1.20 | 1.22 | 1.10 |
| <i>F</i> (000) | 328 | 1208 | 904 |
| <i>μ</i> /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 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 9, -13 ≤ <i>l</i> ≤ 13 | 0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 17, -21 ≤ <i>l</i> ≤ 20 | 0 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 15, -20 ≤ <i>l</i> ≤ 20 |
| Reflections collected | 2979 | 5708 | 3681 |
| Independent reflections | 2979 | 5446 (<i>R</i> _{int} = 0.149) | 3456 (<i>R</i> _{int} = 0.107) |
| Reflections with <i>I</i> > 2σ(<i>I</i>) | 2012 | 2506 | 1654 |
| No. variables | 145 | 316 | 255 |
| <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)] | 0.061 | 0.101 | 0.098 |
| <i>wR</i> 2 (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 | <i>T</i> _{max} = 1.00, <i>T</i> _{min} = 0.75 | — | — |
| Maximum shift/e.s.d. | 0.001 | 0.006 | 0.25 |

with $7 < \theta < 10^\circ$. 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 86²⁹ 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 SiMe₃ group on N, and the other SiMe₃ 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.

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